ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

PREPARATION OF BLOCK COPOLYMER VIA DIELS-ALDER REACTION OF MALEIMIDE- AND ANTHRACENE- END FUNCTIONALIZED POLYMERS

M. Sc. Thesis by

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Department : Polymer Science and Technology

Programme: Polymer Science and Technology

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MALEİMİDE VE ANTRASEN SONLU FONKSİYONEL POLİMERLERİN DİELS-ALDER REAKSİYONUYLA BLOK KOPOLİMERLER SENTEZİ

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LIST of SYMBOLS

ATRP	**:** Atom Transfer Radical Polymerization
SFRP	**:** Stable Free Radical Polymerization
RAFT	**:**Reversible Addition-Fragmentation Chain Transfer Polymerization
DA	**:** Diels-Alder
St	**:** Styrene
MMA	**:** Methyl methacrylate
***t*BA**	**:** *Tert*-butyl acrylate
PS	**:** Polystyrene
PMMA	**:** Polymethyl methacrylate
P*t*BA	**:** Poly*tert*-butyl acrylate
R_m and R_n	**:** Propagating Radical
P_n and P_m	**:** Terminated Macromolecules
LFRP	**:** Living Free Radical Polymerization
CTA	**:** Chain Transfer Agent
TEMPO	**:** 2, 2, 6, 6- Tetramethylpiperidinoxy
PDI	**:** Polydispersity
DP	**:** Degree of Polymerization
PRE	**:** Persistent Radical Effect
M_t^n	**:** Transition metal
L	**:** Ligand
M_w/M_n	**:** The Molecular Weight Distribution
k_a	**:** Rate constant of activation
k_d	**:** Rate constant of deactivation
k_p	**:** Rate constant of propagation
THF	**:** Tetrahydrofuran
DMAP	**:** 4-dimethylaminopyridine
DCC	**:** *N*,*N*-dicyclohexylcarbodiimide
DPTS	**:** 4-dimethylamino pyridinium-4-toluene sulfonate
PMDETA	**:** *N*,*N*,*N*$'$,*N*$''$,*N*$'''$- pentamethyldiethylenetriamine
PEG	**:** Poly(ethylengylycol)
GPC	**:** Gel Permeation Chromotography
NMR	**:** Nuclear Magnetic Resonance Spectroscopy
DSC	**:** Differantial Scanning Calorimetry
UV	**:** Ultra Violet Spectrophotometer

PREPARATION OF BLOCK COPOLYMERS VIA DİELS-ALDER REACTION OF MALEIMIDE- AND ANTHRACENE- END FUNCTIONALIZED POLYMERS

SUMMARY

Accurate control of polymerization process to give polymers with well defined architecture is becoming increasingly important aspect of polymer chemisry. Clasically, the control of macromolecular architecture is only achieved by anionic and cationic polymerization techniques. Recently, the controlled / living radical polymerizations have been utilized for the synthesis of well-defined, narrow polydispersity polymers. Among them atom transfer radical polymerization (ATRP), which has been the subject of many researhs, involves the reversible activation and deactivation of initiator organic halides by redox reaction metal complex.

The Diels-alder reaction generally provides simple, efficient and clean procedure to generate new bonds by inter or intramolecular coupling and represents one of the most usefull synthetic methodes in organic chemistry. In this [4+2] reaction, a dieneophile adds typically to a conjugated diene to give a cylic product called an adduct. One interesting feature of this reaction is its thermal reversibility which implies that its equilibrium can be easily displaced toward the reagents by heating. (Retro Diels-Alder)

The Diels-Alder reaction has been used frequently as a method of protection for a double bond or other functional group. Modification can then be made on other functional groups, and the alkene can be regenerated in a thermal retro DA reaction. The preparations of the DA adducts and the subsequent reductions went cleanly. The final step, the retro DA reaction, proceeded in variable yield depending upon the diene used in the initial step and upon the thermolysis conditions.

Reversible DA reactions between reactive dienes and dieneophiles are well studied. In particular, the reaction between substitutied furans and maleimides has been frequently utilized in the preparation of thermally responsive polymers. This is primarily due to ease of adduct formation and dissociation occurs at elevated temperatures. ($< 90\ ^{o}$ C)

MALİIMİDE VE ANTRASEN SONLU FONKSİYONEL POLYMERLERDEN DİELS-ALDER REAKSİYONUYLA BLOK KOPOLİMERLER SENTEZİ

ÖZET

İyi tanımlanmış mimariye sahip polimerlerin kontrollü polymerizasyon yöntemleriyle eldesi polimer kimyasında gittikçe artan bir öneme sahiptir. Klasik olarak makromoleküler mimarinin kontrolü yalnızca yaşayan anyonik ve katyonik polimerizasyon teknikleri ile başarılabilmektedir. Son yıllarda iyi tanımlanmış düşük polidispersiteye sahip polimerin sentezinde kontrollü / yaşayan polimerizasyon yöntemleri kullanılmaktadır. Bu yöntemler içinde birçok araştırmaya konu olan atom transfer radikal polimerizasyon ATRP metal 7 amin komplekslerinin redoks reaksiyonuna dayanan ve tersinir olarak başlatıcı alkil halojenürlerin aktivasyonu ve deaktivasyonunu içeren bir mekanizma üzerinde yürür.

Moleküller arası veya molekül içi çiftleşmeyle yeni bağlar oluşturmak için Diels-Alder reaksiyonu basit, etkili ve temiz prosedürler sağlar ve organik kimyadaki en kullanışlı sentetik metotlardan biridir. [4+2] reaksiyonu, katılma ürünü olarak isimlendirilen siklik ürünü vermesi için bir dienofil tipik olarak bir konjuge diene katılır.

Diels-Alder reaksiyonu çoğunlukla çift bağ ve fonksiyonel grup içeren koruma metodu olarak kullanılır. Değişim diğer fonksiyonel gruplar içinde yapılabilir ve ısısal geri DA reaksiyonunda alken tekrardan oluşturulabilinir. DA katılma ürününün hazırlanması ve sonraki azalmalar çokça görülebilir. Geri DA reaksiyonu, termoliz koşulları ve başlangıç basamağındaki diene bağlı olarak değişik verimlerde ilerler.

Reaktif dien ve dienofil arasındaki tersinir DA reaksiyonları iyi yürür. Özellikle substitue furanlar ve maleimideler arasındaki bu reaksiyon ısıya duyarlı polimerlerin oluşmasında kullanılır. Katılma ürününün oluşumu oda sıcaklığında, parçalanması ise yüksek sıcaklıklarda oluşur. ($< 90\ ^{o}$ C)

1. INTRODUCTION

In recent years, the use of the controlled/living radical polymerization (CRP) techniques for the synthesis of well-defined, narrow polydispersity polymers has increased fast because of the variety of applicable monomers and more tolerant experimental conditions than the living ionic polymerization routes require. The reversible addition fragmentation chain transfer (RAFT) polymerization [1] , the nitroxide-mediated free radical polymerization [2] (NMP), and the metal mediated controlled / living radical polymerization often called as atom transfer radical polymerization [3-5] (ATRP) are versatile methods for the controlled/living radical polymerizations. However, the latter two cases turned out to be more extensive. One of the advantages of CRP methods when compared with conventional free radical polymerization is the control of the molecular weight and chain end functionality. A wide range of functionality may be introduced into a polymer chain using a hetero-functional initiator if one of the functional groups remains intact during the polymerization. This has provided the synthesis of well-defined block copolymers by a sequential two-step or one pot polymerization method without any chemical transformation or protection of initiating sites. In this point of view, using this strategy, a number of block copolymers have been prepared by combination of different polymerization mechanisms, such as ATRP-NMP [6,7] , ATRP-living ring opening polymerization (ROP) [8-11] , NMP-ROP [8,9,12,13], ATRP-living cationic polymerization.[14] On the other hand, there have been alternative routes for the preparation of block copolymers. One of the routes is that 1,3-dipolar cycloadditions, such as reactions between azides and alkynes or nitriles, are named “click reactions”. [15,16] More recently, Hest et al.[17] successfully prepared polystyrene (PS)-b-poly(methyl methacrylate) (PMMA), poly(ethylene glycol) (PEG)-b-PMMA, and PEG-b-PS block copolymers via using click chemistry strategy between azide- and alkyne-end functionalized homopolymers. Here both PS and PMMA homopolymers were obtained by ATRP method.

Second strategy is the Diels-Alder (DA) reaction, [4+2] system, that generally consists of a coupling of a diene and a dienophile by intra- or intermolecular reaction.[18] Recently, DA reaction has attracted much attention based on the macromolecular chemistry particularly providing new materials. [19-25] More recently, our group carried out the synthesis of ABC type miktoarm star terpolymer with PEG-PS-poly(tert-butylacrylate)(PtBA) arms via DA reaction of maleimide- and anthracene-end functionalized polymers. [26] The end group functionality of PS and PtBA was introduced by utilizing functionalized initiators in ATRP or NMP routes.

As an extension of our previous work, here, we report DA reaction strategy for the preparation of diblock copolymers containing PEG, PS, PMMA or PtBA blocks by a reaction of maleimide end functionalized-PEG, -PMMA, or -PtBA with anthracene end functionalized-PS or -PEG. Here PS, PMMA or PtBA polymers were achieved by ATRP route using various functional initiators. On the other hand, maleimide and anthracene functionalities were introduced into PEG by esterification of monohydroxy PEG with the corresponding carboxylic acid derivatives.

2. THEORETICAL PART

2.1 Controlled/ ‘‘Living” Free Radical Polymerizations

Living polymerization was first defined by Szwarc [27] as a chain growth process without chain breaking reactions (transfer and termination). Such a polymerization provides end-group control and enables the synthesis of block copolymers by sequential monomer addition. However, it does not necessarily provide polymers with molecular weight (MW) control and narrow molecular weight distribution (MWD). Additional prerequisites to achieve these goals include that the initiator should be consumed at early stages of polymerization and that the exchange between species of various reactivities should be at least as fast as propagation [28-30]. It has been suggested to use a term controlled polymerization if these additional criteria are met [31]. This term was proposed for systems, which provide control of MW and MWD but in which chain breaking reactions continue to occur as in RP. However, the term controlled does not specify which features are controlled and which are not controlled. Another option would be to use the term ‘‘living’’ polymerization (with quotation marks) or ‘‘apparently living,’’ which could indicate a process of preparing well-defined polymers under conditions in which chain breaking reactions undoubtedly occur, as in radical polymerization [32,33].

Conventional free radical polymerization techniques are inherently limited in their ability to synthesize resins with well-defined architectural and structural parameters. Free radical processes have been recently developed which allow for both control over molar masses and for complex architectures. Such processes combine both radical techniques with living supports, permitting reversible termination of propagating radicals. In particular, three controlled free radical polymerizations have been well investigated. Each of these techniques is briefly presented below and all are based upon

early work involving the use of initiator-transfer-agent-terminators to control irreversible chain termination of classical free radical process.

Conventional free radical polymerization (FRP) has many advantages over other polymerization processes. FRP does not require stringent process conditions and can be used for the (co)polymerization of a wide range of vinyl monomers. Nearly 50 % of all commercial synthetic polymers are prepared using radical chemistry, providing a spectrum of materials. However, the major limitation of FRP is poor control over some of the key elements of the process that would allow the preparation of well-defined polymers with controlled molecular weight, polydispersity, composition, chain architecture, and site-specific functionality [34].

Living polymerization is defined as a polymerization that undergoes neither termination nor transfer. A plot of molecular weight vs conversion is therefore linear, as seen in Figure 1.1, and the polymer chains all grow at the same rate, decreasing the polydispersity. The propagating center at 100 % conversion still exists and can be further reacted, which can allow novel block, graft, star, or hyperbranched copolymers to be synthesized. Living polymerizations have been realized in anionic processes where transfer and termination are easy to suppress. Due to the favorable coupling of two radical propagating centers and various radical chain transfer reactions, the design and control of a living radical processes is inherently a much more challenging task. The living process of radical polymerization involves the equilibration of growing free radicals and various types of dormant species. By tying up a great deal of the reactive centers as dormant species, the concentration of free radicals decreases substantially and therefore suppresses the transfer and termination steps. These reactions are also denoted as controlled /living polymerizations rather than as true living polymerizations because transfer and termination are decreased but not eliminated. Three processes, NMP, ATRP, and RAFT, will now be introduced. [35]

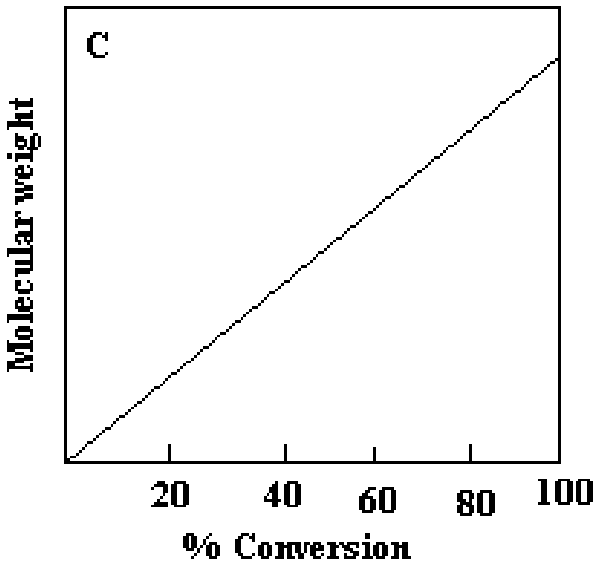


Figure 1.1. Molecular weight vs conversion graph of a typical living polymerization .

Living free radical polymerizations, although only about a decade old, have attained a tremendous following in polymer chemistry. The development of this process has been a long-standing goal because of the desire to combine the undemanding and industrial friendly nature of radical polymerizations with the power to control polydispersities, architectures, and molecular weights that living processes afford. A great deal of effort has been made to develop and understand different living free radical polymerization (LFRP) methods. The methods at the forefront fall into one of three categories: atom transfer radical polymerization (ATRP), nitroxide mediated polymerization (NMP), and reversible addition fragmentation chain transfer (RAFT) [35].

2.1.1 Reversible-Addition Fragmentation Chain Transfer (RAFT)

The most recent report of a controlled/"living" free radical polymerization has been reported by Haddleton and co-workers as well as Thang et al. Reversible addition-fragmentation chain transfer (RAFT) is achieved by performing a free radical polymerization in the presence of dithio compounds, which act as efficient reversible addition-fragmentation chain transfer agents. Much like the first two routes, the rapid switching mechanism between dormant and active chain ends affords living polymerization character [36].

Reversible addition-fragmentation chain transfer (RAFT) incorporates compounds, usually dithio derivatives, within the living polymerization that react with the propagating center to form a dormant intermediate. The dithio compound can release the alkyl group attached to the opposite sulfur atom which can then propagate with the monomer.

The greatest advantage to RAFT is the incredible range of polymerizable monomers. As long as the monomer can undergo radical polymerization, the process will most likey be compatible with RAFT. However, there are many major drawback that arise when using this process. The dithio end groups left on the polymer give rise to toxicity, color, and odor and their removal or displacement requires radical chemistry. Also, the RAFT agents are expensive and not commercially available. Another drawback is that the process requires an initiator, which can cause undesired end groups and produce too many new chains which can lead to increased termination rates [35].

2.1.2 Nitroxide-Mediated Living Free Radical (NMP)

Nitroxide –mediated living free radical polymerization (NMP) belongs to a much larger family of processes called stable free radical polymerizations. In this type of process, the propagating species (Pn°) reacts with a stable radical (X°) as seen in Scheme 2. The resulting dormant species (Pn-X) can then reversibly cleave to regenerate the free radicals once again. Once Pn° forms it can then react with a monomer, M, and propagate further. The most commonly used stable radicals have been nitroxides, especially 2,2,6,6-tetramethylpiperidinoxy (TEMPO). The 2,2',6,6'- tetramethylpiperidine-1-oxyl radical (TEMPO) was used as the nitroxide component in these initial studies. The alkoxyamine is formed in situ during the polymerization process. Shortly thereafter, it was shown that low molecular weight alkoxyamines such as styryl-TEMPO can be used as initiators/regulators for the controlled living radical polymerization of styrene [37]. Although NMP is one of the simplest methods of living free radical polymerization (LFRP), it has many disadvantages. Many monomers will not polymerize because of the stability of the dormant alkoxyamine that forms. Also, since the reaction is kinetically slow, high temperatures and bulk solutions are often required. Also, the alkoxyamine end groups are difficult to transform and require radical chemistry [38].

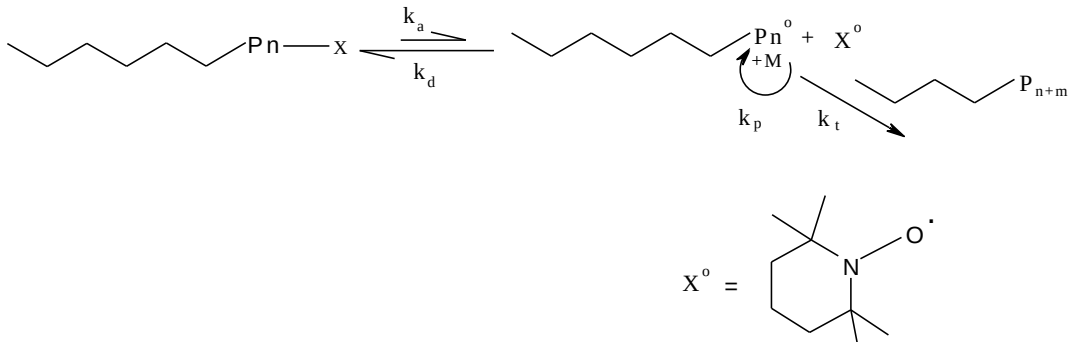


Figure 1.2. Mechanism for nitroxide-madiated living free radical polymerization.

The key to the success is a reversible thermal C═O bond cleavage of a polymeric alkoxyamine to generate the corresponding polymeric radical and a nitroxide. Monomer insertion with subsequent nitroxide trapping leads to chain-extended polymeric alkoxyamine. The whole process is controlled by the so called persistent radical effect (PRE) [39]. The PRE is a general principle that explains the highly specific formation of the cross-coupling product (R_1–R_2) between two radicals R_1 and R_2 when one species is persistent (in NMP the nitroxide) and the other transient (in NMP the polymeric radical), and the two radicals are formed at equal rates (guaranteed in NMP by thermal C═O bond homolysis). The initial buildup in concentration of the persistent nitroxide, caused by the self termination of the transient polymeric radical, steers the reaction subsequently to follow a single pathway, namely the coupling of the nitroxide with the polymeric radical. First, nitroxide mediated polymerizations of styrene were conducted using conventional free radical initiators in the presence of free nitroxide and monomer.[40]. In general better results are obtained using preformed alkoxyamines. Defined concentration of the initiator allows a better control of the targeted molecular weight using this approach. Based on the mechanism depicted in Figure 1.2 it is obvious that the equilibrium constant *K* between the dormant alkoxyamine and the polymeric radical and nitroxide is a key parameter of the polymerization process. The equilibrium constant *K* is defined as *k*a/*k*d (*k*a = rate constant for alkoxyamine C═O bond homolysis; *k*d = rate constant for trapping of the polymeric radical with the given nitroxide). Various parameters such as steric effects, H-bonding and polar effects influence the *K*-value. [41]. Since the first TEMPO-mediated polymerizations many nitroxides and their

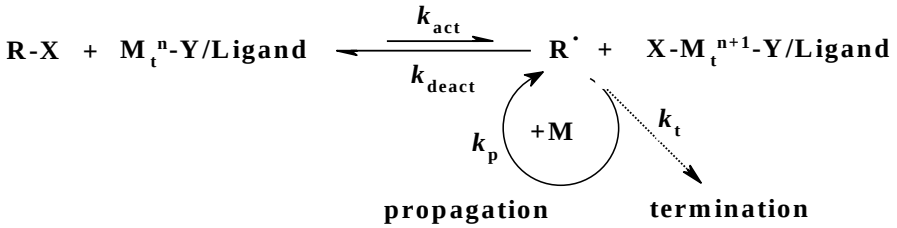
corresponding alkoxyamines have been prepared and tested in NMP. Due to space limitation we cannot give an overview of all alkoxyamines tested so far [42].

The most popular nitroxide used for NMP in the past has been TEMPO. However, TEMPO is limited in the range of monomers which are compatible to polymerize by NMP, mostly due to the stability of the radical. Hawker et. al. recently discovered that by replacing the α-tertiary carbon atom with a secondary carbon atom, the stability of the nitroxide radical decreased which lead to an increased effectiveness in polymerization for many monomers in which TEMPO was uneffective . While TEMPO and TEMPO derivatives are only useful for styrene polymerizations, the new derivatives permit the polymerization of acrylates, acrylamides, 1,3-dienes, and acrylonitrile based monomers with very accurate control of molecular weights and low polydispersities. Another family of nitroxides that have shown to have the same success are phosphonate derivatives designed by Gnanou et.al [43].

The chain end functionalization of polymers synthesized by NMP is a significant problem because dormant chains containing alkoxyamines can regenerate terminal radicals which can depolymerize at high temperatures. A very interesting chain end functionalization process has also been discovered by Hawker et. al. which involves the controlled monoaddtion of maleic anhydride or maleimide derivatives to the alkoxyamine chain end. The alkoxyamine can then be easily eliminated and other functional groups can be introduced. This process relies on the resistance of maleic anhydride or maleimide derivatives to homopolymerize and the ability of the precurser to reform the olefin by elimination of the hydroxylamine [44].

2.1.3 Atom Transfer Radical Polymerization

Atom transfer radical polymerization (ATRP) is a living radical polymerization process utilizing transition-metal complexes as catalysts to mediate the propagation of the polymerization. It is a very versatile process and can synthesize a wide spectrum of polymers with controlled structures. Atom transfer radical polymerization (ATRP) is one of the most convenient methods to synthesize well-defined low molecular weight polymers [45]. A general mechanism for ATRP is given below.



Firstly, initiation should be fast, providing a constant concentration of growing polymer chains. Secondly, because of the persistent radical effect, the majority of the growing polymer chains are dormant species that still presence the ability to grow because a dynamic equilibrium between dormant species. By keeping the concentration of active species of propagating radicals sufficiently low through the polymer, termination is suppressed. ATRP is a radical process that full fills these requirements by using a transition metal in combination with a suitable ligand [46].

Atom transfer radical polymerization (ATRP) involves first a reduction of the initiator by a transition metal complex forming a radical initiating species and a metal halide complex. The reactive center can then initiate the monomer, which can then propagate with additional monomer or abstract the halide from the metal complex forming a dormant alkyl halide species. The alkyl halide species is then activated by the metal complex and propagates once more.

ATRP can be used on a large number of monomers and requires ambient reaction conditions. The reaction is uneffected by the precence of O_2 and other inhibitors. Also, the alkyl halide end groups can be easily transformed by S_N^1, S_N^2, or radical chemistry. The major drawback to ATRP is that a transition metal catalyst which is used must be removed which after polymerization and possibly recycled. Future work in this field includes the removal and recycling of the catalyst as well as the design of catalysts that react with a larger range of monomers [35].

A transition metal complex, e.g. copper (I) bromide, undergoes an one-electron oxidation with simultaneous homolytic abstraction of the halogen atom from a dormant species (e.g. carbon–halide bond) to generate a radical. The radical propagates monomers with the activity similar to a conventional free radical. The radical is very quickly deactivated to its dormant state—the polymer chain terminally capped with a

halide (e.g. P–Br) group. Since the deactivation rate constant is substantially higher than that of the activation reaction $K_{eq} = K_{act} / K_{deact} \sim 10^{-7}$; each polymer chain is protected by spending most of the time in the dormant state, and thereby the permanent termination via radical coupling and disproportionation is substantially reduced. In a well-controlled ATRP, only several percents of the chains become dead via termination.

This process occurs with a rate constant of activation, k_{act}, and deactivation, k_{deact}. Polymer chains grow by the addition of the intermediate radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation k_p. Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination.

Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of polymerization. This process generates oxidized metal complexes, $X\text{-}M_t^{n+1}$, as persistent radicals to reduce the stationary concentration of termination [47]. Polydispersities in ATRP decrease with conversion, with the rate constant of deactivation, k_{deact}, and also with the concentration of deactivator. The molecular conversion and the amount of initiator used, $DP = \Delta[M]/[I]_0$; polydispersities are low, $M_w / M_n < 1{,}3$ [48].

The ATRP system is consisting of the monomer, initiator, and catalyst composed of transition metal species with any suitable ligand.

ATRP has been successfully used in living polymerizations of a wide range of monomers, such as styrenic monomers, acrylates, methacrylates, (meth)acrylamides, acrylnitrile and vinyl chloride in bulk, solution using organics or water as solvents, and emulsion, supercritical carbon dioxide, producing polymers with well-controlled molecular weights and structures. For example, polystyrene with polydispersity as narrow as those of PS standards synthesized by living anionic polymerization was obtained by coppercatalyzed ATRP [49].

The amount of the initiator in the ATRP determines the final molecular weight of the polymer at full monomer conversion. Multifunctional initiators may provide chain

growth in several directions. The main role of the initiator is to determine the number of growing polymer chains. If initiation is fast and transfer and termination negligible, then the number of growing chains is constant and equal to the initial initiator concentration. The theoretical molecular weight or degree of polymerization (DP) increases reciprocally with the initial concentration of initiator in a living polymerization.

$$\mathbf{DP = [M]_0 / [I]_0 \times Conversion}$$

In ATRP, alkyl halides (RX) are typically used as the initiator and the rate of the polymerization is first order with respect to the concentration of RX. To obtain well-defined polymers with narrow molecular weight distributions, the halide group X, must rapidly and selectively migrate between the growing chain and the transition-metal complex.

Initiation should be fast and quantitative with a good initiator. In general haloganated alkanes, benzylic halides, α-haloesters, α-haloketones, α-halonitriles and sulfonyl halides are used as ATRP initiators [50].

The most frequently used initiator types used in the atom transfer radical polymerization systems are, 1-Bromo-1-phenyl ethane (Styrene), 1-Chloro-1-phenyl ethane (Styrene), Ethyl-2-bromo propionate (Methyl methacrylate) and Ethyl-2-bromo isobutyrate (Methyl methacrylate). Two parameters are important for a successful ATRP initiating system; first, initiation should be fast in comparison with propagation. Second, the probability of side reactions should be minimized [50].

Transition metal catalysts are the key to ATRP since they determine the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. The main effect of the ligand is to solubilize the transition-metal salt in organic media and to regulate the proper reactivity and dynamic halogen exchange between the metal center and the dormant species or persistent radical. Ligands, typically amines or phosphines, are used to increase the solubility of the complex transition metal salts in the solution and to tune the reactivity of the metal towards halogen abstraction. Linear amines with ethylene linkage like tetramethylethylenediamine (TMEDA), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA), and 1,1,4,7,10,10 hexamethyltriethylenetetramine (HMTETA) were synthesized and examined for ATRP

as ligands [51]. Reasons for examining of these type of ligands are, they are not expensive, due to the absence of the extensive π-bonding in the simple amines, the subsequent copper complexes are less colored and since the coordination complexes between copper and simple amines tend to have lower redox potentials than the copper-bpy complex, the employment of simple amines as the ligand in ATRP may lead to faster polymerization rates.

Catalyst is the most important component of ATRP. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst. First, the metal center must have at least two readily accessible oxidation states separated by one electron. Second the metal center should have reasonable affinity toward a halogen. Third the coordination sphere around the metal should be expandable upon oxidation to selectively accommodate a (pseudo)-halogen. Fourth the ligand should complex the metal relatively strong.

The most important catalysts used in ATRP are; Cu(I)Cl, Cu(I)Br, $NiBr_2(PPh_3)_2$, $FeCl_2(PPh_3)_2$, $RuCl_2(PPh_3)_3$/ $Al(OR)_3$.

ATRP can be carried out either in bulk, in solution or in a heterogeneous system (e.g., emulsion, suspension). Various solvents such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide and many others have been used for different monomers. A solvent is sometimes necessary especially when the obtained polymer is insoluble in its monomer [52].

2.2 Block Copolymers

A diblock copolymer is a linear-chain molecule consisting of two sub-chains joined covalently to each other. One of the sub-chains is made of monomers of type A and the other of type B. Block copolymers comprise a particularly interesting class of materials constituted by two or more blocks of different polymer chains where each block presents sequences of 50–1000 repetitive units, linked by covalent bonds. When the blocks are miscible, these materials are homogeneous and exhibit disordered domains with

properties intermediate with respect to the constituent blocks. Applications in materials science, molecular biology, electronics and pharmacy are being currently investigated [53]. At present, in addition to the ionic copolymerization techniques, new polymerization techniques are employed [54] which allow handling even hundreds of monomers, a capability not shown by existing processes, thus opening a way for new polymeric materials. Molecular simulations offer a particularly useful way to explore the morphology and other physical properties of these materials and to make predictions that may be of interest in improving existing synthetic processes. Recent advances in molecular dynamics methodology [55] together with the high performance of modern computers have made possible to routinely study the microscopic details of chemical processes in condensed phase. These are advances in molecular simulations which permit to study systems in the mesoscopic domain [56] and, in particular, make possible to describe very large polymeric systems.

Block copolymers are useful in many applications where a number of different polymers are connected together to yield a material with hybrid properties. For example, thermoplastic elastomers are block copolymers containing a rubbery matrix (polybutadiene or polyisoprene) containing glassy hard domains (often polystyrene). The block copolymer, a kind of polymer alloy, behaves as a rubber at ambient conditions, but can be moulded at high temperatures due to the presence of the glassy domains that act as physical crosslinks. In solution, attachment of a water soluble polymer to an insoluble polymer leads to the formation of micelles in amphiphilic block copolymers. The presence of micelles leads to structural and flow characteristics of the polymer in solution that differ from either parent polymer. A block copolymer molecule contains two or more polymer chains attached at their ends. Linear block copolymers comprise two or more polymer chains in sequence, whereas a star block copolymer comprises more than two linear block copolymers attached at a common branch point. Polymers containing at least three homopolymers attached at a common branching point have been termed mixed arm block copolymers, although they can also be viewed as multigraft copolymers. In the following, block copolymers prepared by controlled polymerization methods only are considered, primarily di- and tri-block copolymers. Multiblock copolymers such as polyurethanes and poly (urethane- ureas) prepared by

condensation polymerisation are not discussed. Whilst these materials do exhibit microphase separation, it is only short range in spatial extent due to the high polydispersity of the polymers. A standard notation for block copolymers is becoming accepted, whereby X-b-Y denotes a diblock copolymer of polymer X and polymer Y. However, sometimes the b is replaced by the full term block, or alternatively is omitted, and the diblock is denoted X-Y. A number of texts covering general aspects of block copolymer science and engineering appeared in the 1970s and 1980s and these are listed elsewhere . More recently, specialised reviews have appeared on block copolymer melts and block copolymer solutions [57].

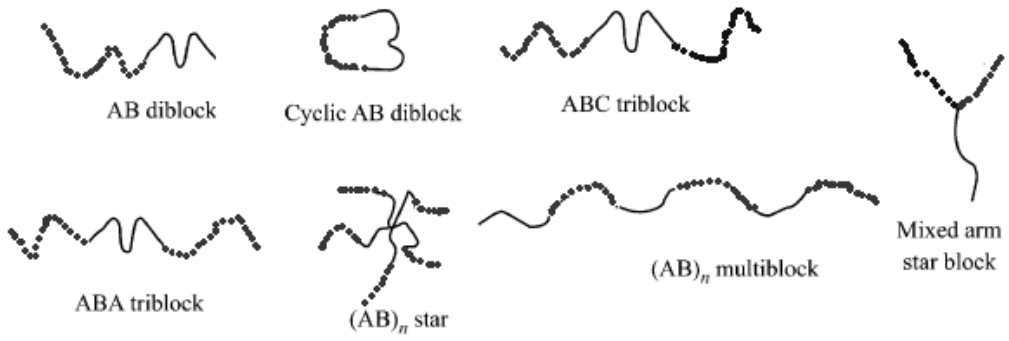


Figure 1.3. Block copolymers architectures.

2.2.1 Synthesis of Block Copolymer

The main techniques for synthesis of block copolymers in research labs around the world are presently anionic polymerization and controlled radical polymerization methods. The older technique of anionic polymerization is still used widely in the industrial manufacture of block copolymers. Cationic polymerization may be used to polymerize monomers that cannot be polymerized anionically, although it is used for only a limited range of monomers. A summary of block copolymer synthesis techniques has been provided by Hillmyer [58].

2.2.1.1. Anionic Polymerization

Anionic polymerization is a well-established method for the synthesis of tailored block copolymers. The first anionic polymerizations of block copolymers were conducted as early as 1956 . To prepare well-defined polymers, the technique is demanding, requiring high-purity starting reagents and the use of high-vacuum procedures to prevent accidental termination due to the presence of impurities. In the lab, it is possible to achieve polydispersitiesMw=Mn < 1:05 via anionic polymerization. The method is also used industrially to prepare several important classes of block copolymers including SBS-type thermoplastic elastomers and polyoxyethylene-*b*-polyoxypropylene-*b*-polyoxyethylene Pluronic amphiphilic copolymers [59].

2.2.1.2. Controlled/ ‘‘Living” Free Radical Polymerizations

Undoubtedly the main advance in block copolymer synthesis in the last decade has been the development of techniques of living radical polymerization (sometimes termed controlled radical polymerization). The principle of controlled radical polymerization methods is to establish a dynamic equilibrium between a small fraction of growing free radicals and a large majority of dormant species. Generated free radicals propagate and terminate as in conventional radical polymerization, although the presence of only a small fraction of radicals prevents premature termination. Among living polymerization methods, atomtransfer radical polymerization (ATRP) has been used most extensively to synthesize block copolymers. Here, the radicals are generated through a reversible redox process catalysed by a transition metal complex that undergoes a one-electron oxidation with the abstraction of a halogen atom from the dormant species. ATRP has been used to prepare AB diblock, ABA triblock and most recently ABC triblock copolymers. To date, the technique has been used to create block copolymers based on polystyrene and various polyacrylates. However, it is possible to synthesize a so-called macroinitiator by other polymerization mechanisms (anionic, cationic, etc.), and use this in the ATRP of vinyl monomers. Examples, such as the anionic polymerization of PEO macroinitiators for ATRP synthesis of PEO/PS block copolymers, are discussed by Matyjaszewski and Xia.

Sequential living cationic polymerization is primarily used to prepare block copolymers containing a vinyl ether block, or polyisobutylene. It can also be coupled with other techniques. However, the range of monomers that may be polymerized by this method is comparatively limited and consequently living cationic polymerization is only used in prescribed circumstances. Ring-opening metathesis polymerization has also been exploited to build blocks from cyclic olefins, especially polynorbornene. The development of ROMP for block copolymer synthesis has recently been facilitated by the introduction of functional-group-tolerant metathesis catalysts by Grubbs [57].

2.3 Diels-Alder Reaction

The Diels-Alder cycloaddition reaction (DA reaction) is one of the most versatile and powerful synthetic transformations in organic chemistry, occupying a position of particular prominence among the carbon-carbon bond forming reactions. Its widespread application is the introduction of up to four new contiguous asymmetric centers with good yields, high selectivity and predictability. In the following, a lot of recent papers will be cited, which should give an overview of recent developments in asymmetric DA reactions. [59]

One of the most efficient methods (high yield, controlled stereochemistry, diverse functionality) to construct rings from smaller fragments is via cycloaddition reactions. The reverse reaction, namely splitting of a ring into smaller fragments is termed a cycloreversion reaction is also an important synthetic tool. (For example, in the present experiment it is the cracking of cyclopentadiene dimer to cyclopentadiene monomer.) The construction of six-membered rings built from a fragment of four atoms linked together by two conjugated double bonds (a diene) and a fragment containing two atoms linked by a double bond or triple bond (a dienophile) is known as the Diels-Alder (D-A) reaction. It is often shorthanded as a [4+2]-p-electron cycloaddition. During the retro-D-A, a six-membered ring is split into a diene (often an aromatic compound) and a homonuclear (alkene, alkyne) or heteronuclear (CO) p bond.

The simplest example of a D-A reaction is the reaction between butadiene and ethylene to form cyclohexene. Both the diene and the dienophile display a very low reactivity.

Please note the very sluggish reaction conditions: high pressure and an unusual high butadiene: ethylene molar ratio.

Nevertheless, a dienophile substituted with electron withdrawing group(s) and/or a diene substituted with electron donor group(s) reacts at lower temperature at atmospheric pressure resulting in cyclohexene derivatives in medium to very high yield. An alternative version is the inverse electron demand D-A reaction in which an electron-rich alkene reacts with an electron-poor diene. The diene must be able to assume s-cis conformation. If the conjugated double bonds are rigidly fixed in the s-trans configuration, the respective diene does not undergo D-A reaction.

Larger rate acceleration (shorter reaction time at room or lower temperature, often with an increase in the regioselectivity) can be achieved using Lewis acid catalysts like $AlCl_3$, Et_2AlCl, BF_3, $B(OAc)_3$, $ZnCl_2$, $SnCl_4$ and $TiCl_4$. Because the Lewis acid coordinates at the Lewis base side of the dienophile, for example, at the carbonyl oxygen of methacrolein, it makes the CO group even more electron-withdrawing and, therefore, more reactive. The crystalline phase (X-ray, see figure below) and in solution structure (Nuclear Overhauser Effect) of the methacrolein boron trifluoride both display an s-trans frame of the,b-enal and the Lewis acid coordinated syn to the lone pair to the formyl proton [60].

Stereochemistry of the D-A reaction.

1. Regioselectivity.
2. Stereoselectivity:

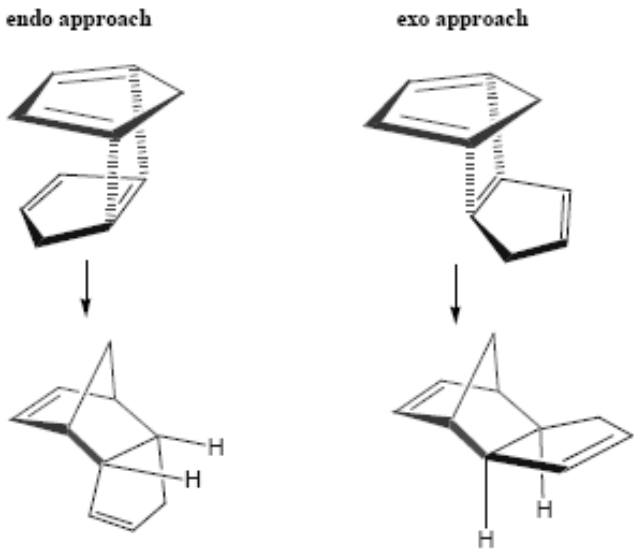
a. Diastereoselective (endo, exo).

b. Enantioselective (R, S).

Unsymmetrical dienes like piperylene react with methyl acrylate to yield two isomeric adducts (two regioisomers) that differ only by the relative orientation of the two substituents, methyl and carbomethoxy, respectively.

In the absence of a catalyst, the endo product is preferentially formed (Alder endo rule). Cycloaddition of methacrolein to cyclopentadiene yields a mixture of exo-CHO-3 and endo-CHO-3 diastereoisomers in a ratio that is dramatically dependent on reaction conditions. For example, at a relatively high temperature and longer reaction time the

aldehyde group shows a preference for the endo position. At a lower temperature and in the presence of a Lewis catalyst the exo diastereoisomer is preponderantly formed. For example, cyclopentadiene, the diene employed in the present experiment, has a limited shelf lifetime at room temperature (8% is converted into its dimer in 4 h and 50% in 24 h) because it reacts with itself to form the endo diastereoisomer:



D-A reactions make simultaneously two carbon-carbon bonds, and if the product lacks a plane of symmetry, they create four stereocenters in the process. Thus, a synthesis of a molecule containing several stereocenters via a Diels-Alder reaction may be particularly efficient, provided that the relative and absolute stereochemistry of the Diels-Alder reaction can be controlled. There is no general way of accomplishing this objective for all types of Diels-Alder reactions, but the catalyst developed recently (1989) in Hisashi Yamamoto's group. (Nagoya University) provide good stereocontrol with a number of useful combinations of substrates.

The regio-and stereoselectivities of Diels-Alder cycloaddition are easily rationalized by examining only the frontier molecular orbitals (F.M.O.) of diene and dienophiles. Frontier orbitals are the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Woodward and Hoffmann pointed out in 1965 that if the cycloaddition is concerted, during the D.-A. reaction the HOMO of the diene interacts in phase (constructive overlap) with LUMO of the dienophile:

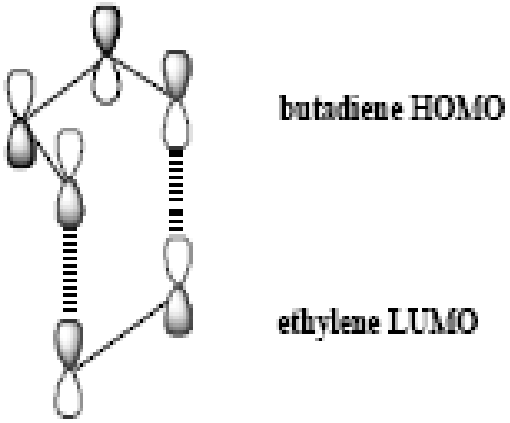


Figure 1.4. In phase interaction of HOMO of butadiene with LUMO of ethylene.

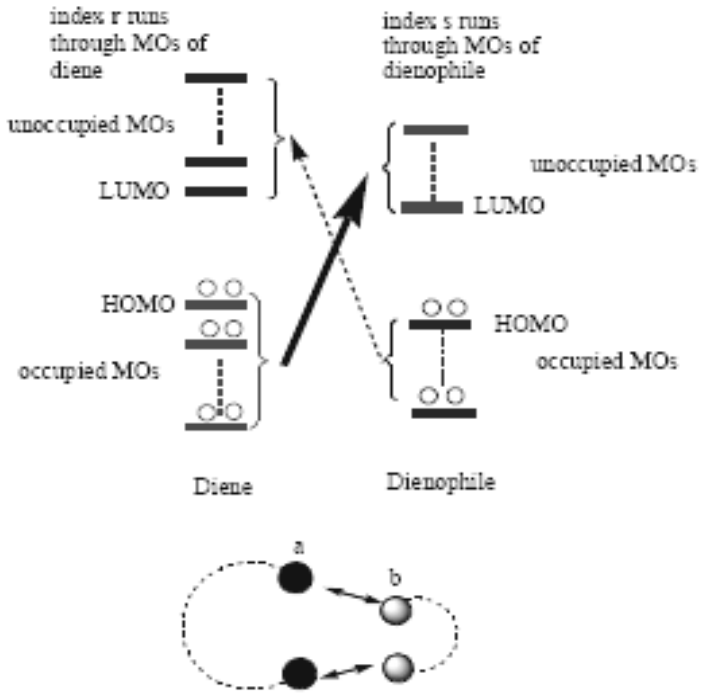


Figure 1.5. Orbitals interaction in a Diels-Alder reactions.

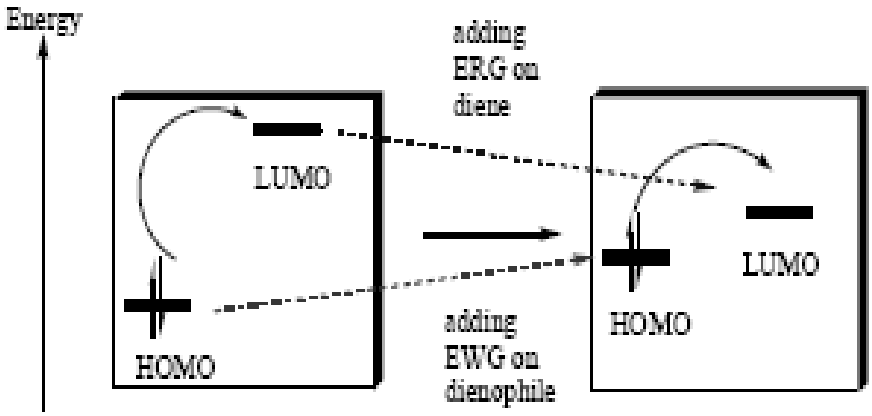
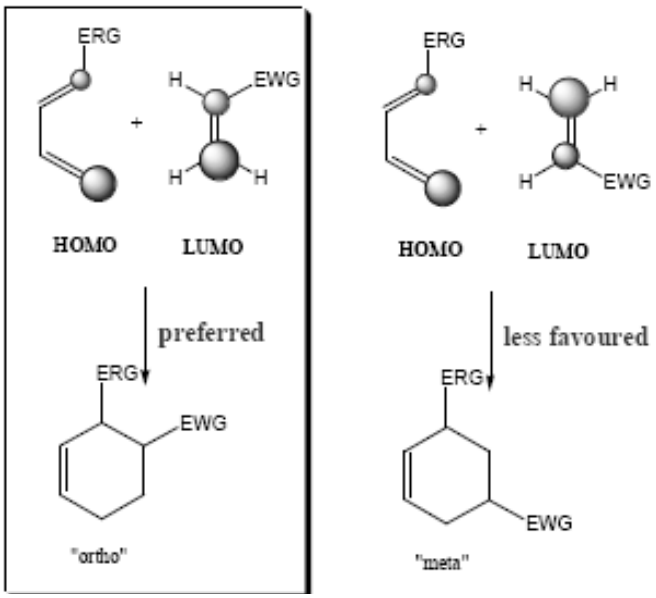


Figure 1.6. Substituents effect on the HOMO-LUMO gap.

Regioselectivity, an acceptable explanation for regioselectivity can be provided by examining the F.O. of a dienophile and diene. If the reaction is uncatalyzed and there is a lack of strong solvent effect, a key factor in orienting the direction of the cycloaddition is the size of the coefficient on the individual atoms that are forming the new bonds. The new bonds are formed preferentially when "large-large" and "small-small" (Houk rule) overlap:



Diastereoselectivity., endo addition is favored as a result of secondary interaction(s) (colored in blue) among the F.M.O. of diene at C_2, C_3 and dienophile at C_3. Secondary interactions will lower the height of the transition state. However, the endo diastereoisomer is less stable (because of steric repulsions) thermodynamically than the

exo isomer. Although the exo isomer requires higher energy of activation, it is more stable thermodynamically. The endo isomer is said to be formed under kinetic control. The exo isomer is formed under thermodynamic control [61].

The Diels-Alder (DA) reaction generally involves the coupling of a "diene" with a "dienophile". A vast array of intra- and intermolecular DA reactions have been studied for both mechanistic and synthetic reasons. One of the many interesting features of the DA reaction is the readiness of many adducts to undergo the reverse reaction when heated to an appropriate temperature, thus regenerating the original reactants. The application of DA chemistry to polymer synthesis, modification, and (reversible) cross-linking has received some attention, but much remains to be done to exploit the potential of the DA reaction to provide access to novel materials [62].

Retro Diels-Alder (RDA) is the reverse reaction of Diels-Alder reaction, and it may produce new compounds. RDA could be used to analyze the primary diene and dienophile. And it can be used as group protection method. Photochemical Diels-Alder additions of chiral 9-anthranyl ethanol derivatives have been conducted giving rise to addition adducts in reasonable yield and excellent diastereoselectivity. Thermal and photochemical retro Diels-Alder additions have also been achieved providing a facile cleavage method for use of this compound as a new chiral auxiliary. Asymmetric synthesis and the novel retro Diels-Alder reaction of a P-chiral sulfonyl-substituted phosphanorbornene was achieved.

Thermally reversible Diels-Alder [4+2] cycloadditions of a diene and dienophile have been used to prepare and modify polymers. Dienes and dieneophile have also been attached as pendant ar end groups on polymer backbones [63].

Reversible DA reactions between reactive dienes and dieneophiles are well studied. In particular, the reaction between substituted furans and maleimides has been frequently utilized in the preparation of thermally responsive polymers. This is primarily due to ease of adduct formation and dissociation. Adduct formation typically occurs at room temperature, and adduct dissociation ocuurs at elevated temperatures [64].

3. EXPERIMENTAL WORK

3.1 Materials

Styrene (St, 99%, Merck), methyl methacrylate (MMA, 99%, Aldrich) and *tert*-butylacrylate (*t*BA, 99%, Aldrich) were passed through basic alumina column to remove inhibitor and then distilled over CaH_2 *in vacuo* prior to use. *N, N, N', N'', N''*-pentamethyldiethylenetriamine (PMDETA, Aldrich) was distilled over NaOH prior to use. Poly(ethylene glycol) (PEG) (*M*n = 550, Acros and *M*n = 5000, Fluka) was dried over anhydrous toluene by azeotropic distillation. 4-dimethylaminopyridinium 4-toluenesulphonate (DPTS) was obtained according to a published procedure. Tetrahydrofuran (THF, 99.8%, J.T. Baker) was dried and distilled over benzophenone-Na. Dichloromethane was purchased from Aldrich and used after distillation over P_2O_5.Other solvents were purified by conventional procedures. All other reagents were purchased from Aldrich and used as received.

3.2 Synthesis of Initiators

3.2.1 Synthesis of 4,10-Dioxatricyclo[5.2.1.0 ^{2,6}]dec-8-ene-3,5-dione (1):

Maleic anhydride (30.0 g, 306 mmol) was suspended in 150 mL of toluene and the mixture warmed to 80 ° C. Furan (33.4 mL, 459 mmol) was added via syringe and the turbid solution stirred for 6 h. The mixture was then cooled to ambient temperature and the stirring stopped. After 1 h, the resulting white crystals were collected by filtration and washed with 2 × 30 mL of petroleum ether. Obtained was 44.4 g (267 mmol, 87 % yield) of as small white needless [65].

3.2.2 Synthesis of 4-(2-Hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.0 ^{2,6}]dec-8-ene-3,5- dione (2):

The anhydride **1** (10.00 g, 60.0 mmol) was suspended in MeOH (150 mL) and the mixture cooled to 0 ° C. A solution of ethanolamine (3.6 mL, 60 mmol) in 30 mL of MeOH was added dropwise (10 min), and the resulting solution was stirred for 5 min

at 0 ° C, then 30 min at ambient temperature, and finally refluxed for 6 h. After cooling the mixture to ambient temperature, the solvent was removed under reduced pressure, and the white residue was dissolved in 150 mL of CH_2Cl_2 and washed with 3 × 100 mL of water. The organic layer was dried over $MgSO_4$ and filtered. Removal of the solvent under reduced pressure furnished an off-white residue that was purified by flash chromatography to give (4.9 g , 25 mmol, 40 % yield) as a white solid [65].

3.2.3 Synthesis of 2-Bromo-2-methyl Propionic Acid 2-(3,5-Dioxo-10-oxa-4-azatricyclo [5.2.1.0 ^{2,6}] dec-8-en-4-yl) Ethyl Ester (3):

A solution of the alcohol **2** (2.00 g, 9.549mmol) and Et_3N (1.441 mL, 10.539 mmol) in 100 mL of THF (the solution remained slightly turbid) was cooled to 0 ° C, and a solution of 2-bromo isobutyryl bromide (1.262 mL, 9.999 mmol) in 25 mL of THF was added dropwise (30 min). The white suspension was stirred for 3 h at 0 °C and subsequently at ambient temperature overnight. The ammonium salt was filtered off and the solvent removed under reduced pressure to give a pale-yellow residue that was purified by flash chromatography . Obtained was 1.86 g (55 % yield) of as a white solid. ^{1}H NMR ($CDCl_3$, O) 6.49 (t, 2H, CH_{vinyl}), 5.23 (t, 2H, CHO), 4.30 (t, 2H, OCH_2), 3.78 (t, 2H, NCH_2), 2.84 (s, 2H, CH9, 1.86 (s, 6H, CH_3). [65]

3.2.4 Synthesis of 2-Bromo-propionic Acid 2-(3,5-dioxo-10-oxa-4 azatricyclo [5.2.1.0 ^{2,6}] dec -8-en-4-yl) Ethyl Ester (4):

A solution of the alcohol **2** (3.00 g, 14.3mmol) and Et_3N (2.156 mL, 15.78 mmol) in 100 mL of THF (the solution remained slightly turbid) was cooled to 0 ° C, and a solution of 2-bromo propionyl bromide (1.89 mL, 17.8 mmol) in 25 mL of THF was added dropwise (30 min). The white suspension was stirred for 1 h at 0 ° C and subsequently at ambient temperature overnight. The ammonium salt was filtered off and the solvent removed under reduced pressure to give a pale-yellow residue that was purified by flash chromatography using CH_2Cl_2 as eluent . Obtained was 4.15 g (84 % yield) of as a white solid. ^{1}H NMR ($CDCl_3$, O) 6.72 (t, 2H, CH_{vinyl}), 4.32 (t, 2H, OCH_2), 3.84 (t, 2H, NCH_2), 1.88 (s, 6H, CH_3).

3.2.5 Synthesis of 9-anthyrylmethyl 2-bromo-2-methyl Propanoate (5):

9-Anthryl methanol (1.5 g, 7.18 mmol) and DMAP (0,175 g, 1,436 mmol) were dissolved in 10 mL of THF, and Et_3N (1,2 mL, 8,6 mmol) was added. The reaction mixture was then cooled to 0 ^{o}C. 2-Bromo-2-methyl propionyl bromide (1,82 g, 7,89 mmol) was added dropwise within 30 minutes. The reaction mixture was stirred over night at room tempeature. The reaction was filtered off, solvent evaporated then extracted with CH_2Cl_2, and saturated aq. $NaHCO_3$. The water phase again extracted with CH_2CL_2, and combined organic phase dried with Na_2SO_4. The solution was concantrated, and the crude product was purified by column chromatography over silica gel eluting with hexane/ethylacetate (10:1) to give the yield 1,78 g (4,97 mmol, %70) as yellow solid. ^{1}H NMR ($CDCl_3$, O) 7.43-8.52 (m, 9 ArH of anthracene), 6.21 (s, 2H, CH_2-O), 1.87 (s, $(CH_3)_2$-C-Br).

3.3 Synthesis of Polymers

3.3.1 Synthesis of PMMA-maleimide (6):

The PMMA-maleimide was prepared by ATRP of MMA. In a 50 mL of Schlenk tube, MMA (5 mL, 46.7 mmol), toluene (5 mL), PMDETA (0.196 mL, 0.94 mmol), CuCl (0.093 g, 0.94 mmol) and **3** (0.336 g, 0.94 mol) were added and the reaction mixture was degassed by three freeze-pump-thaw cycles and left in vacuum. The tube was then placed in an oil bath thermostated at 40 ^{o} C for a given reaction time. Afterward the dark-blue polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated in methanol. The polymer was dried for 24 h in a vacuum oven at 50 ^{o} C.

3.3.2 Synthesis of PS-anthracene (7):

PS-anthracene was prepared by ATRP of St. In a 50 mL of Schlenk tube, St (15 mL, 130 mmol), PMDETA (0.136 mL, 0.655 mmol), CuBr (0.0939 g, 0.655 mmol) and **5** (0.234 g, 0.655 mmol) were added and the reaction mixture was degassed by three freeze-pump- thaw cycles and left in vacuum. The tube was then placed in a thermostated oil bath at 110 ^{o} C for 45 min. The dark-green polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated in methanol. The polymer was dried for 24 h in a vacuum oven at 50 ^{o} C. [M]o/[I]o = 200; [I]o:[CuBr]:[PMDETA] = 1:1:1; conv. % = 14;

*M*n,theo = 3280; *M*n,NMR = 3240; *M*n,UV = 3430; *M*n,GPC = 3400; *M*w/*M*n = 1.13.

3.3.3 Synthesis of P*t*BA-maleimide (8):

The P*t*BA-maleimide was prepared by ATRP of *t*BA. In a 50 mL of Schlenk tube, *t*BA (2 mL, 13.6 mmol), PMDETA (0.0284 mL, 0.136 mmol), CuBr (0.0195 g, 0.136 mmol) and **4** (0.0468 g, 0.136 mmol) were added and the reaction mixture was degassed by three freeze-pump-thaw cycles and left in vacuum. The tube was then placed in a thermostated-oil bath at 40 ^{o} C for 480 min. The dark-green polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated into water-methanol (1:4). The polymer was dried for 24 h in a vacuum oven at 50 ^{o} C. [M]o/[I]o = 100; [I]o:[CuBr]: [PMDETA]= 1:1:1; conv. % = 20; *M*n,theo = 2560; *M*n,NMR = 2600; *M*n,GPC = 3500; *M*w/*M*n = 1.16.

3.4 Synthesis of PEG-maleimide

3.4.1 Synthesis of 4-maleimido-benzoic Acid (9) :

Compound **9** was synthesized by modification of literature procedure. In a three necked flask provided with a reflux condenser, 4-amino benzoic acid (13,7 g, 100 mmol) was dissolved in DMF (150 ml). Under mechanical stirring, a solution of maleic anhydride (21,56 g, 220 mmol) in DMF (80 ml) was added dropwise through a dropping funnel under N_2 atmosphere during 30 min. After the addition, the thick suspension was stirred at room temperature for 1 h. Afterward acetic anhydride (100 ml, 336 mmol), sodium acetate (2,5 g, 30 mmol) were added. The reaction mixture was heated at 45 ^{o} C for 2 h. then overnight at room temperature under stirring. After cooling to room temperature, the reaction mixture was poured into ice-cold water (100 ml). The product was filtered off and dried in a vacuum oven. The crude product was recrystallized from water -ethanol (1:4) to give the pure product 11 g (% 51)yield) as white solid.

3.4.2. Synthesis of 4-maleimido-benzoylchloride (10) :

4-maleimido-benzoic acid **9** (5 g, 23,2 mmol) was dissolved in excess thionyl chloride under nitrogen atmosphere. After the mixture was refluxed for overnight, excess thionyl chloride was removed under reduced pressure and the product was crystallized from benzene to give **10** as yellow solid (Yield: 4,23 g, 78 %).

3.4.3. Esterification of PEG with 4-maleimido-benzoylchloride (11) :

PEG (M_n= 550) (2 g, 3.63 mmol) was dissolved in 10 mL of THF, and Et_3N (0.8 mL, 5.44 mmol) was added. The reaction mixture was cooled to 0 ^{o}C and a solution of 4-maleimidobenzoylchloride **10** (1.7 g, 7.26 mmol) in 10 mL of THF was added drop wise within 30 minutes. The reaction mixture was stirred overnight at room temperature. After filtration off the salt, the solution was concentrated and the viscous brown color product was purified by column chromatography over silica gel eluting with CH_2Cl_2/ethylacetate (1:1) and then with CH_2Cl_2/MeOH (10:1) to give **11** as viscous yellow oil (Yield: 1.76 g, 65%). $M_{n,theo}$ = 750; $M_{n,NMR}$ = 732; $M_{n,GPC}$ = 740; M_w/M_n = 1.07. ^{1}H NMR ($CDCl_3$, O) 8.14 (d, 2H, OC=OAr*H*), 7.49 (d, 2H, Ar*H*NC=O), 6.88 (s, 2H, NC=OC*H*=C*H*), 4.48 (t, 2H, PEG-OCH_2CH_2OC=O), 3.82 (t, 2H, PEG-OCH_2CH_2OC=O), 3.67-3.62 (m, 4H, -OCH_2CH_2- of PEG), 3.54 (t, 2H, CH_3-O-CH_2CH_2-O), 3.37 (s, 3H, CH_3-OCH_2CH_2).

3.5. Synthesis of PEG-anthracene

3.5.1 Synthesis of succinic acid mono-anthracen-9-ylmethyl-ester (12) :

9-Anthryl methanol (4.16 g, 20 mmol) was dissolved in 150 mL of CH_2Cl_2. To the reaction mixture were added Et_3N (14 ml, 100 mmol) and DMAP (2.44 g, 20 mmol). The succinic anhydride (8 g, 80 mmol) was added and stirred overnight at room temperature. The reaction solution was poured into ice-cold water (150 ml) and extracted with CH_2Cl_2. The organic phase again extracted with 1M HCl (150 ml).Water phases extracted with CH_2Cl_2. Combined organic phase dried over Na_2SO_4 and concentrated to yield 5.85 g (117 mmol, %95) as green solid..

3.5.2 Synthesis of PEG-anthracene (13) :

PEG (*M*n = 5000) (1 g, 0.2 mmol) was dissolved in 10 mL of dry dichloromethane along with 1 (0.185 g, 0.6 mmol). Dimethylaminopyridine (DMAP) (0.002 g, 0.02

mmol) and DPTS (0.0314 g, 0.1 mmol) were added in that order. After stirring 5 minutes, dicyclohexylcarbodiimide (DCC) (0.124 g, 0.6 mmol) dissolved in 5 mL of CH_2Cl_2 was added to a reaction mixture and was stirred overnight at room temperature. After filtration off the urea byproduct, it was precipitated in diethyl ether and dried in vacuum. This procedure was repeated two times to give pure PEG-anthracene as white solid, 0.83 g (yield: 79%). *M*n,theo = 5300, *M*n,NMR = 5360, *M*n,UV = 4800, *M*n,GPC = 5300, *M*w/*M*n = 1.13. 1 H NMR (CDCl3, O) 1 H NMR (CDCl3, O) 8.5 (s, 1H, Ar*H*), 8.30 (d, 2H, Ar*H*), 8.02 (d, 2H, Ar*H*), 7.6-7.45 (m, 4H, Ar*H*), 6.15 (s, 2H, CH_2-Ar), 4.14 (t, 2H, PEG-OCH$_2$CH_2OC=O), 3.62 (m, 4H, -OCH_2CH_2- of PEG), 3.35 (s, 3H, CH_3-OCH$_2$CH$_2$), 2.63 (4H, C=OCH_2CH_2C=O).

3.6 Model Diels-Alder Reaction between 3 and 5 (14):

The compound **3** (0.250 g, 6.98 X 10 $^{-4}$ mol) was added to **5** (0.249 g, 6.98 X 10 $^{-4}$ mol) in 10 mL of toluene. The mixture was bubbled with nitrogen for 30 min and then refluxed for 24 h at 110 ^{o} C. The solvent was removed and the remaining product was purified by column chromatography over silica gel eluting once with hexane/ethylacetate (1:4) and then ethylacetate to give adduct **14** (0.485 g; 97 %). ^{1} H NMR (CDCl3, O) 7.42-7.19 (m, 8H, Ar*H*), 5.61 and 5.43 (dd, 2H, bridge-head-CH_2OC=O), 4.78 (s, 1H, C*H*, bridge-head proton), 3.64 (t, 2H, C=OOCH_2CH$_2$N), 3.38-3.33 (m, 4H, C=OOCH$_2$CH_2N and CH$_2$NC=OC*H*-*CH*, as bridge protons), 1.97 (d, 6H, CBr(C*H*3)$_2$), 1.86 (s, 6H, CBr(C*H*3)$_2$).

3.7 Diels - Alder Reactions

3.7.1 Preparation of PEG-*b*-PS copolymer via DA reaction of PEG-maleimide and PS-anthracene (15) :

PS-anthracene (0.250 g, 7.3 X 10 $^{-2}$ mmol) was added to 0.054 g of PEG-maleimide (7.7 X 10 $^{-2}$ mmol) in 15 mL of toluene. The mixture was bubbled with nitrogen for 1 h and then refluxed for 48 h under nitrogen. The reaction mixture was evaporated under high vacuum. The efficiency of block copolymerization (DA reaction) was found to be 97.5 % by UV measurement based on the remaining PS-anthracene in reaction mixture. Next, reaction mixture was purified by dissolving in THF and then precipitating in methanol. *M*n,NMR = 4100; *M*n,GPC = 4700; *M*w/*M*n = 1.07.

3.7.2 Preparation of PMMA-*b*-PS copolymer via DA reaction of PMMA-maleimide and PS-anthracene (16) :

A solution of PMMA-maleimide (run no 2 in Table 1) (0.217 g, 3.23 X 10^{-2} mmol) in 5 mL of toluene was added to 0.110 g of PS-anthracene (3.23 X 10^{-2} mmol) in 5 mL of toluene. The mixture was bubbled with nitrogen for 1 h and then refluxed for 120 h under nitrogen. The reaction mixture was evaporated under high vacuum. The efficiency of block copolymerization (DA reaction) was found to be 98.5 % by UV measurement based on the remaining PS-anthracene in reaction mixture. Next the mixture was dissolved in THF and then precipitating in methanol and redissolved in THF and reprecipitated in cyclohexane. *M*n,NMR = 8850; *M*n,GPC = 9500; *M*w/*M*n = 1.13.

3.7.3 Preparation of P*t*BA-*b*-PS copolymer via DA reaction of P*t*BA-maleimide and PS-anthracene (17):

A solution of P*t*BA-maleimide (0.2 g, 5.71 X 10^{-2} mmol) in 5 mL of toluene was added to (0.194 g, 5.71 X 10^{-2} mmol) of PS-anthracene in 5 mL of toluene. The mixture was bubbled for 1h with nitrogen. The mixture was then refluxed under nitrogen for 120 h. at 110 ^{o} C. The reaction mixture was evaporated under high vacuum. The efficiency of block copolymerization (DA reaction) was found to be 92 % by UV measurement based on the remaining PS-anthracene in reaction mixture. Next the mixture was dissolved in THF and poured into methanol-water and extracted with CH2Cl2. *M*n,NMR = 5350; *M*n,GPC = 4400; *M*w/*M*n = 1.30.

3.7.4 Preparation of PMMA-*b*-PEG block copolymer via DA reaction of PMMA-maleimide and PEG-anthracene (18):

A solution of PMMA-maleimide (run no 1 in Table 1) (0.250 g, 4.17 X 10^{-2} mmol) in 5 mL of toluene was added to (0.22 g, 4.17 X 10^{-2} mmol) of PEG-anthracene in 5 mL of toluene. The mixture was bubbled with nitrogen and refluxed for 120 h. at 110 ^{o} C. The reaction mixture was evaporated under high vacuum. The efficiency of block copolymerization (DA reaction) was found to be 93 % by UV measurement based on the remaining PEG-anthracene in reaction mixture. The mixture was dissolved in THF and poured into diethyl ether two times. The remaining product was redissolved in THF and reprecipitated in acetonitrile. *M*n,NMR = 11150; *M*n,GPC = 8500; *M*w/*M*n = 1.11.

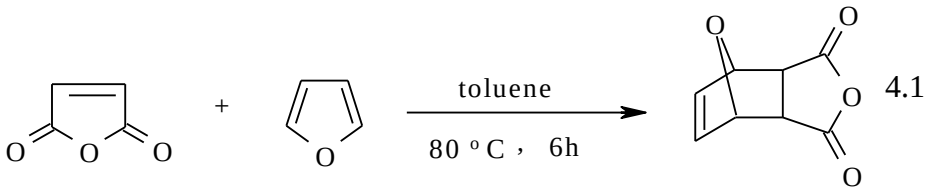
3.8 Characterization

The ^{1}H-NMR spectra was recorded on a Bruker spectrometer (250 MHz for proton) in $CDCl_3$ solution using tetramethylsilane (TMS) as an internal standart.Gel Permeation Chromatography (GPC) measurements were carried out with an Agilent Model 1100 instrument consists of pump, refractive index dedector, UV dedectors and four Waters Styragel columns (HR 5E, HR 4E, HR 3 and HR 2). THF was used as eluent at flow rate of 0.3 mL/min. at 30 ^{o}C. The molecular weights of the polymers were calculated with the aid of polystyrene standarts (Polymer Laboratories). All polymers obtained were dried overnight under vacuum and the conversions were determined by gravimetrically. UV spectra were recorded on a Perkin Elmer Lambda 2 spectrometer in CH_2Cl_2. Differential Scanning Calorimetry (DSC) was measured on a DSC Q100 (TA Instruments) at a heating rate of 10 ^{o}C/min under nitrogen atmosphere. All data were collected from a second heating cycle and the glass transitions were calculated as a midpoint of thermograms.

4. RESULTS and DISCUSSION

4.1 Synthesis of Initiators

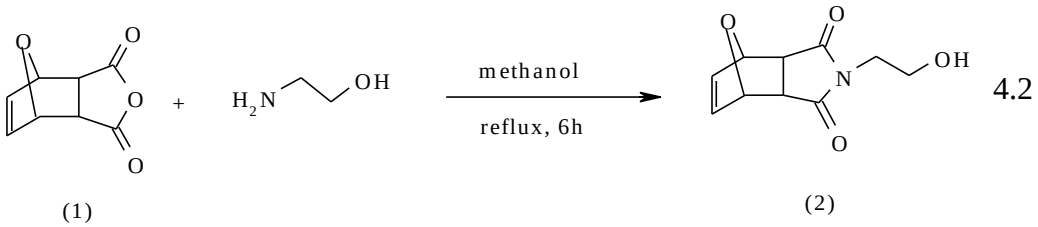
First of all, maleic anhydride and furan were reacted in toluene at reflux temperature for 6 h to give 4,10-Dioxatricyclo[5.2.1.0 ^{2,6}]dec-8-ene-3,5-dione **1**. The anhydride **1** was obtained as small white needless.



4.1

(1)

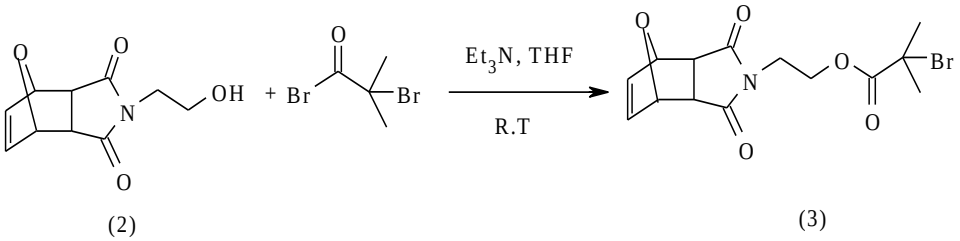
The reaction of the anhydride **1** was then carried out to give the 4-(2-Hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5- dione **2.** In this reaction, the anhydride **1** was suspended in MeOH and a solution of ethanolamine in MeOH was added at 0 ^{o} C, then the mixture refluxed for 6h. Finally, compound **2** was obtained as a white solid.



4.2

(1) (2)

Subsequent this reaction, compound **2** and Et_3N was mixed in THF. Additionally, a solution of 2-bromo isobutyryl bromide was added in THF at 0 ^{o} C. After this process, the reaction was carried out at ambient temperature overnight. Finally, 2-Bromo-2-methyl propionic acid 2-(3,5-Dioxo-10-oxa-4- azatricyclo [5.2.1.0 ^{2,6}] dec-8-en-4-yl) ethyl ester **3** was obtained as a white solid. The ^{1}H NMR spectrum of the compound, **3,** is shown in Figure 4.1.



4.3

(2) (3)

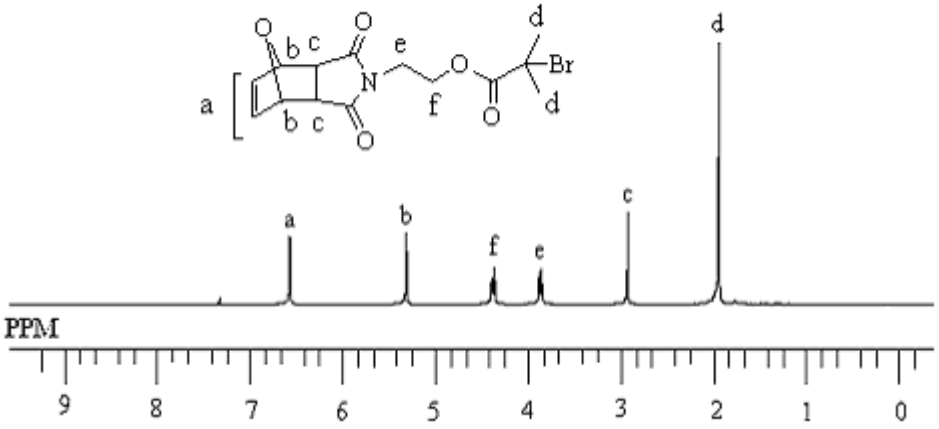
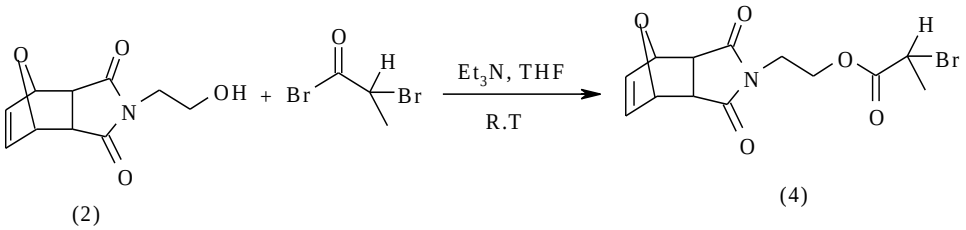


Figure 4.1. The ^{1}H NMR spectrum of 2-Bromo-2-methyl propionic acid 2-(3,5-Dioxo-10-oxa-4- azatricyclo [5.2.1.0 ^{2,6}] dec-8-en-4-yl) ethyl ester in $CDCl_3$

2-bromo-propionic acid 2-(3,5-dioxo-10-oxa-4 azatricyclo [5.2.1.0 ^{2,6}] dec -8-en-4-yl) ethyl ester **4** was synthesized by using compounds **1** and **2**. In this reaction, compound **2** and Et_3N was mixed in THF. In the final step, a solution of 2-bromo propionyl bromide in THF was added at 0 ^{o}C and the reaction carried out at ambient temperature overnight. As aresult of this process, compound **4** obtained as a white solid. The ^{1}H NMR spectrum of the compound, **(4),** is shown in Figure 4.2.



4.4

(2) (4)

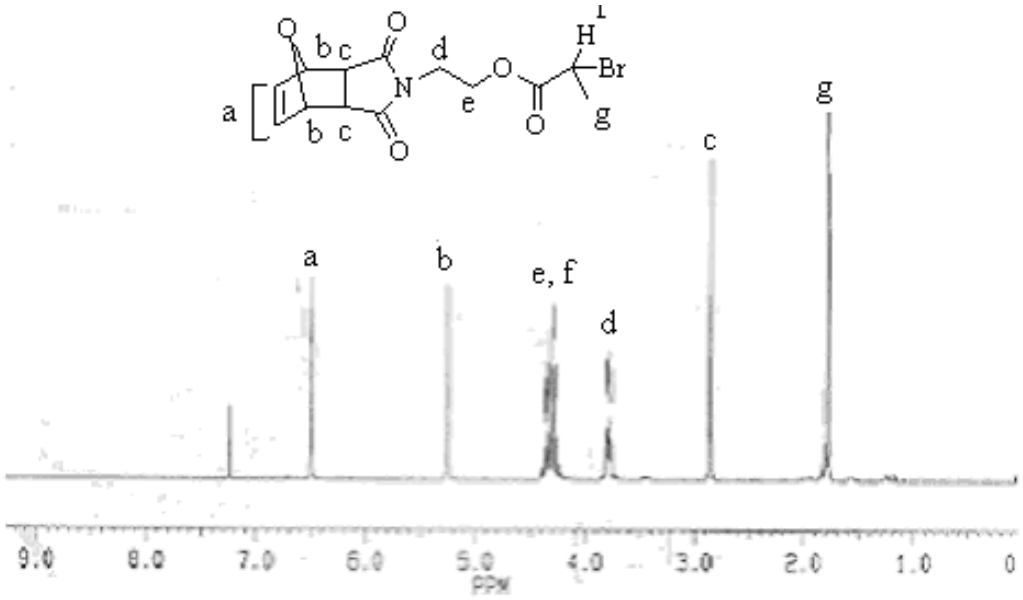
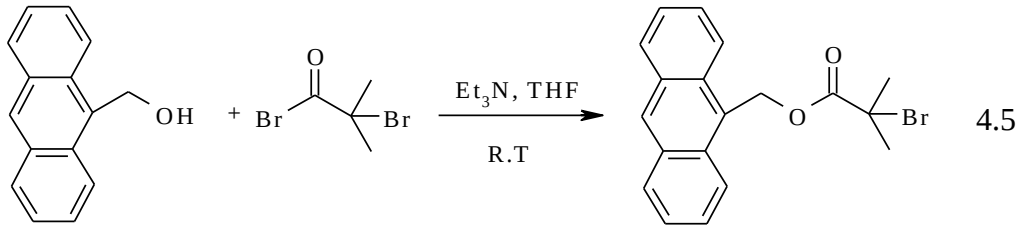


Figure 4.2. The ^{1}H NMR spectrum of 2-bromo-propionic acid 2-(3,5-dioxo-10-oxa-4 azatricyclo [5.2.1.0 ^{2,6}] dec -8-en-4-yl) ethyl ester in $CDCl_3$

In order to occur 9-anthyrylmethyl 2-bromo-2-methyl propanoate **5**, 9-Anthryl methanol and catalytic amount of DMAP dissolved in THF. Then Et_3N was added. 2-Bromo-2-methyl propionyl bromide was dropped in this mixture at 0 ^{o}C. In the final step, this reaction was carried out at romm temperature for overnight. Finally, product **5** was obtained as ayellow solid. The ^{1}H NMR spectrum of the compound, **5,** is shown in Figure 4.3.



4.5

(5)

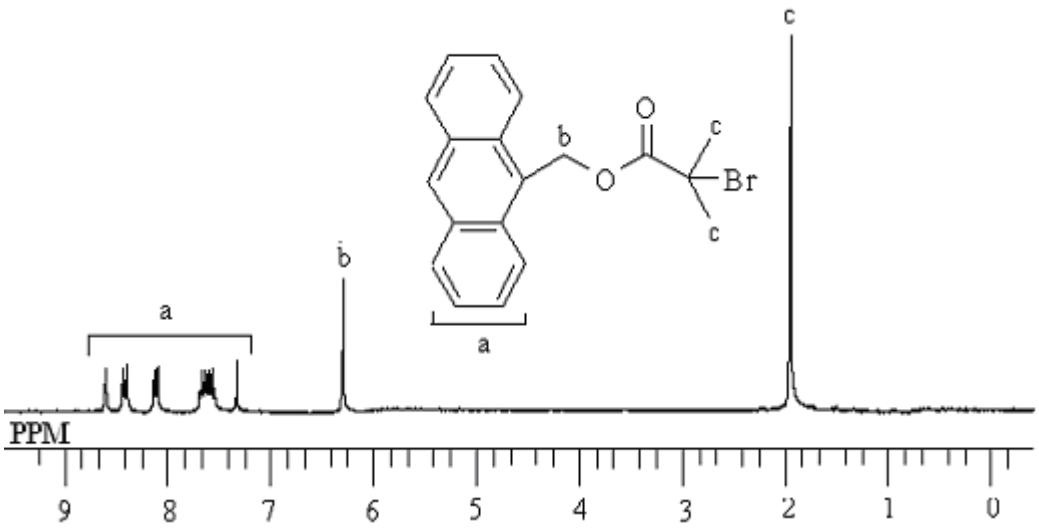


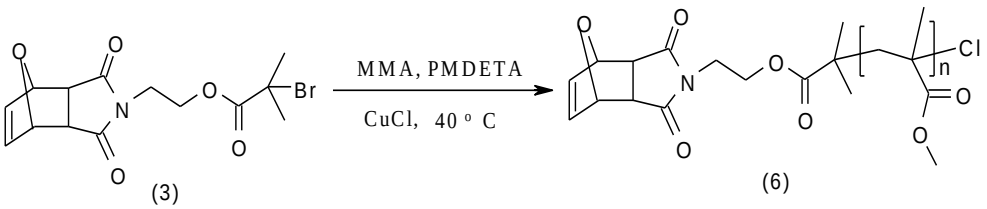
Figure 4.3. The ^{1}H NMR spectrum of 9-anthyrylmethyl 2-bromo-2-methyl propanoate in $CDCl_3$

4.2 Synthesis of Polymers:

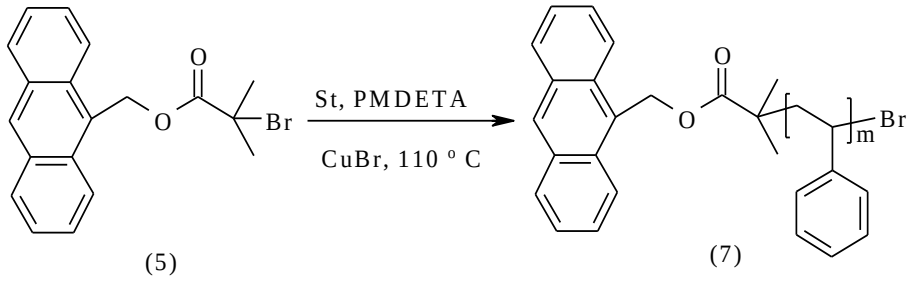
The anthracene or maleimide end functionality was introduced into PMMA, PS, and P*t*BA by using proper initiators in ATRP of MMA, St, and tBA. However, maleimide functionality could not be directly inserted to polymer backbone due to copolymerization of maleimidegroup with MMA or tBA. To avoid this circumstance, the protected maleimide initiators were used in ATRP. Deprotection of maleimide functionalized polymers (retro-DA) were in situ carried out during the block copolymerization stage (DA reaction). Thus, obtained end functionalized polymers were used to give block copolymer via DA reactions performing between maleimide and anthracene functionalities.

4.2.1 Preparation of PMMA-maleimide, PS-anthracene, and P*t*BA-maleimide by ATRP:

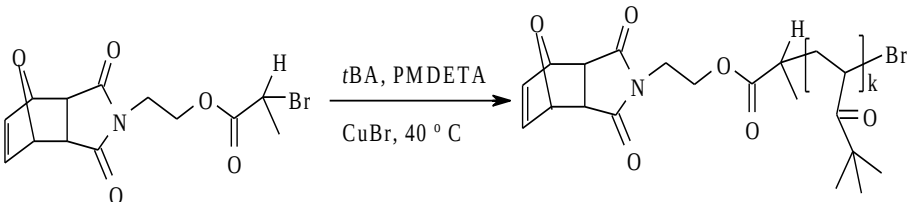
PMMA-maleimide, PS-anthracene, and PtBA-maleimide were obtained by ATRP of MMA, St, and *t*BA using initiators **3**, **4**, and **5.**



4.6



(5) (7) 4.7



(4) (8) 4.8

The theoretical molecular weight of polymers were calculated by using following equation: *M*n,theo = ([M]o/[I]o) X conversion % X molecular weight (MW) of monomer + MW of initiator. The NMR number-average molecular weight (*M*n,NMR) of PMMA-maleimide was determined from a ratio of integrated signals at 3.58 ppm (OCH3 protons of MMA) to 6.5 ppm (vinyl end protons). (The ^{1}H NMR spectrum of PMMA-maleimide, **6,** is shown in Figure 4.4). To this value added was the molecular weight of **3**. *M*n,NMR values were consistent with those of the number-average molecular weight calculated by GPC (*M*n,GPC) (Table 4.1). The initiating efficiencies are in the range of 0.38-0.41.

Table 4.1. The synthesis and characterization of PMMA-maleimide obtained from compound **3**.

Run No[a]	$[M]_o/[I]_o$	Time (min.)	Conv (%)	$M_{n,theo}$	$M_{n,GPC}$[b]	Initiation Efficiency (f)[c]	M_w/M_n	$M_{n,NMR}$
1	50	240	39	2300	6000	0.38	1.12	5500
2	50	300	48	2800	6700	0.41	1.13	6300

[a]$[2]_o$: [CuBr]: [PMDETA] = 1: 1: 1. The polymerization was carried out at 40 ° C. MMA / toluene = 1 (v/v). [b]Calculated from GPC calibrated with linear poly(methyl methacrylate) standarts. [c]Calculated from $f = M_{n,theo}/ M_{n,GPC.}$

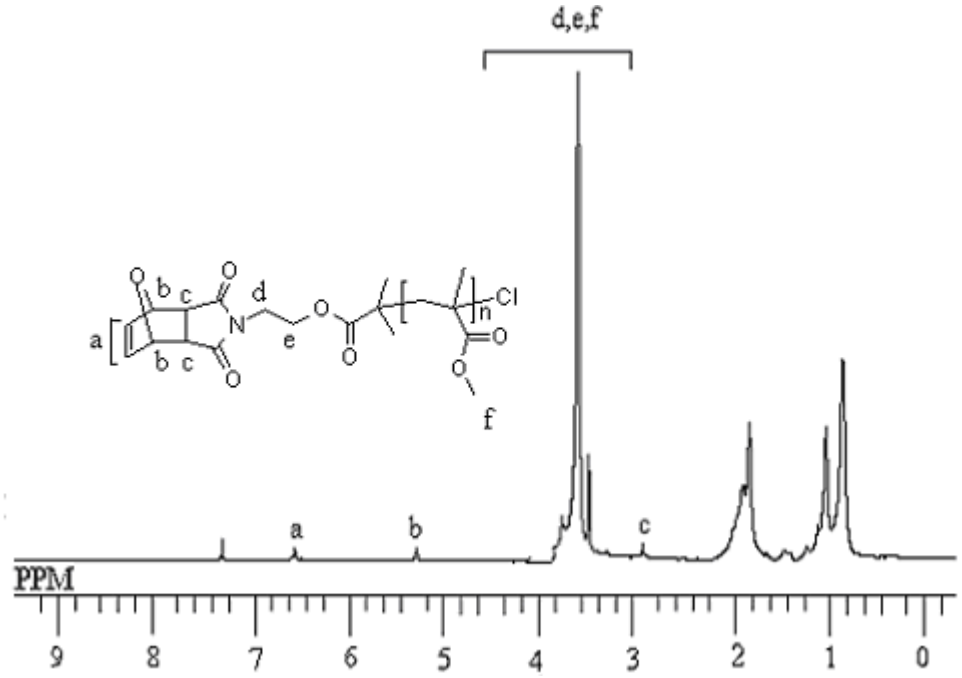


Figure 4.4. The ^{1}H NMR spectrum of PMMA-maleimide in$CDCl_3$

$M_{n,NMR}$ value of PS-anthracene was calculated by comparing of the integrals of the aromatic protons of PS at 6.5-7.5 ppm and that of two protons of anthracene end group at 7.9 ppm. The ^{1}H NMR spectrum of PS-anthracene **7,** is shown in Figure 4.5. It was observed that $M_{n,theo}$ $M_{n,NMR,}$ $M_{n,GPC}$ and the number-average molecular weight calculated by UV ($M_{n,UV}$) were in good agreement.

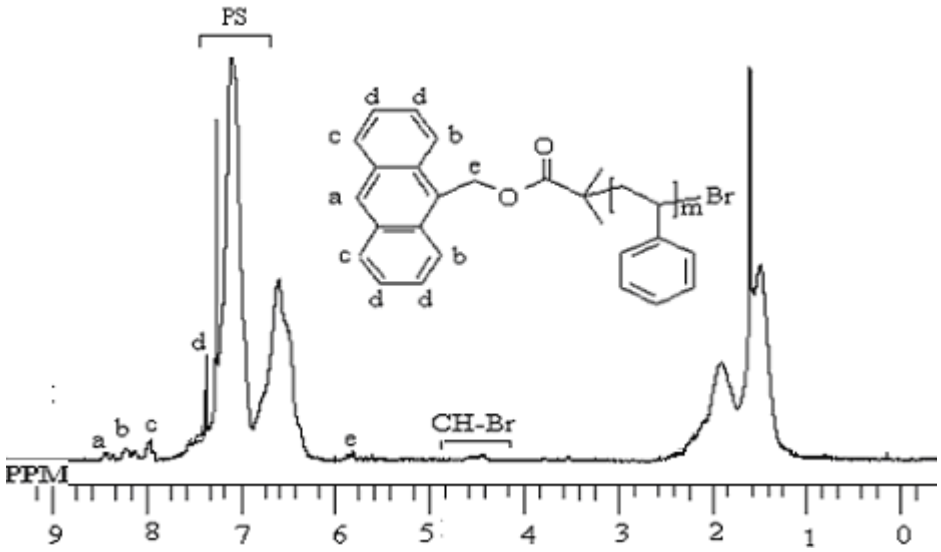


Figure 5. The ^{1}H NMR spectrum of PS-anthracene in $CDCl_3$

$M_{n,NMR}$ of P*t*BA-maleimide was determined by comparing of the integrals of the vinyl end protons at 6.5 ppm and that of the tert-butyl group of P*t*BA at 1.4 ppm. The ^{1}H NMR spectrum of P*t*BA **8**, is shown in Figure 4.6.

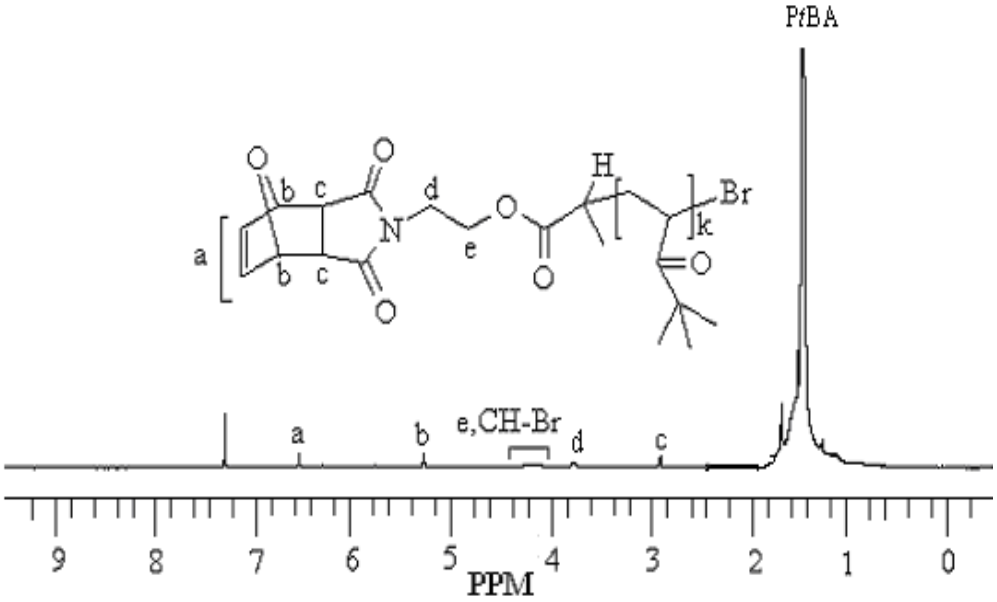
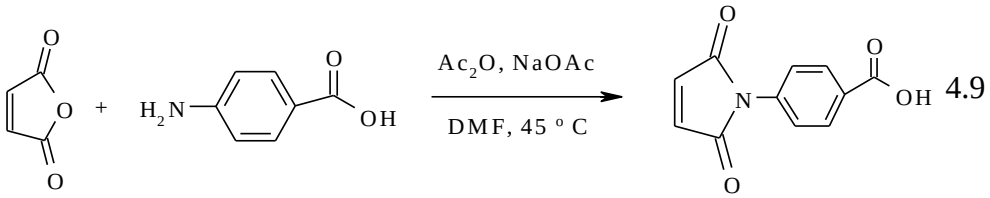
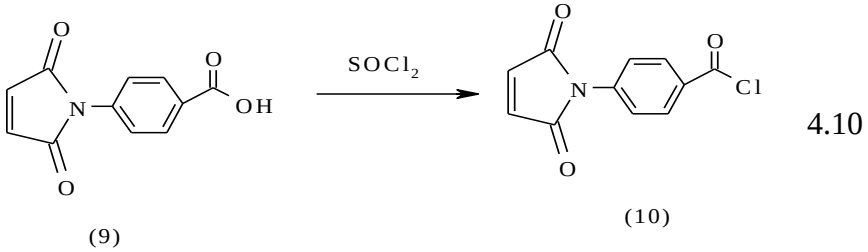


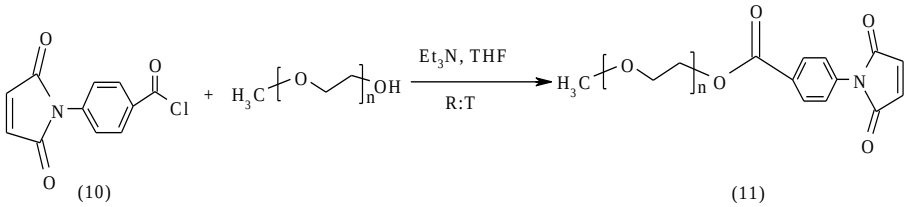
Figure 4.6. The ^{1}H NMR spectrum of P*t*BA in $CDCl_3$

4.3 Synthesis of PEG-maleimide

Esterification reaction between PEG (550) and 4-maleimido-benzoylchloride **10** was carried out in THF. Et_3N was added then the mixture was cooled to 0 ^{o}C. After this process, 4-maleimidobenzoylchloride **10** was added in THF. The reaction mixture was sticarried out for overnight at room temperature. Finally, compound **11** was obtained as viscous yellow oil. The ^{1}H NMR spectrum of , **11,** is shown in Figure 4.7.







4.11

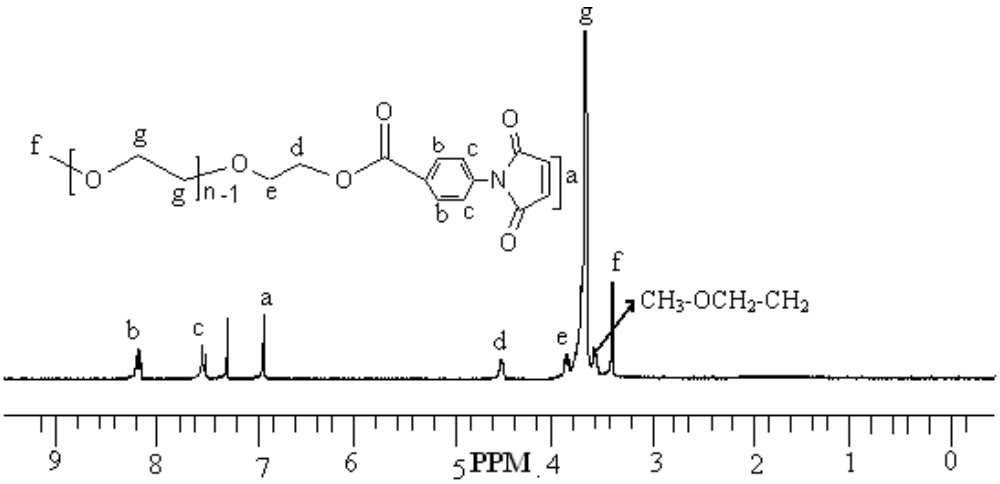
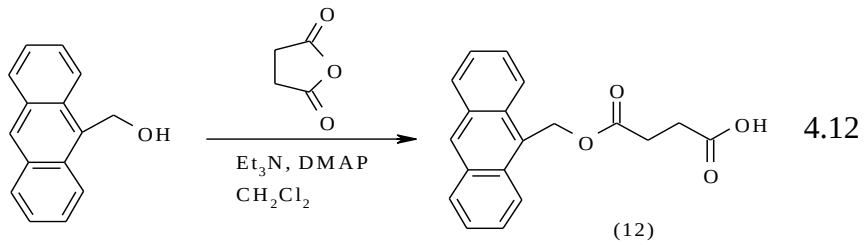


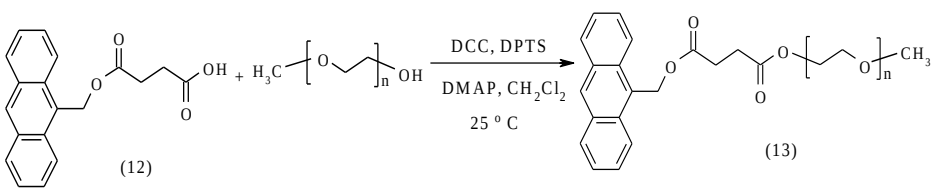
Figure 4.7. The ^{1}H NMR spectrum of PEG-maleimide in $CDCl_3$

4.4 Synthesis of PEG-anthracene

PEG-anthracene was synthesized by using PEG (*M*n = 5000), catalytic amount of DMAP (dimethylaminopyridine), and catalytic amount of DPTS (dimethylamino-4-toluene-sulfonate) in CH_2Cl_2. Additionally, DCC (dicyclohexylcarbodiimide) in CH_2Cl_2. This reaction was carried out overnight at room temperature. Finally, compound **13** was obtaiened as white solid. The ^{1}H NMR spectrum of , **13,** is shown in Figure 4.8.



4.12



4.13

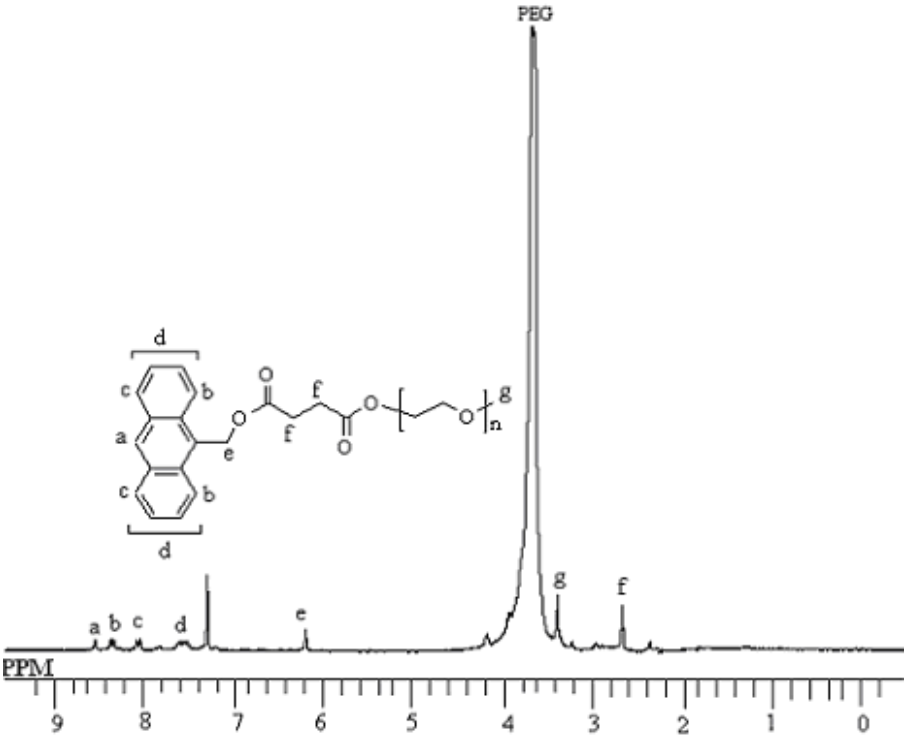
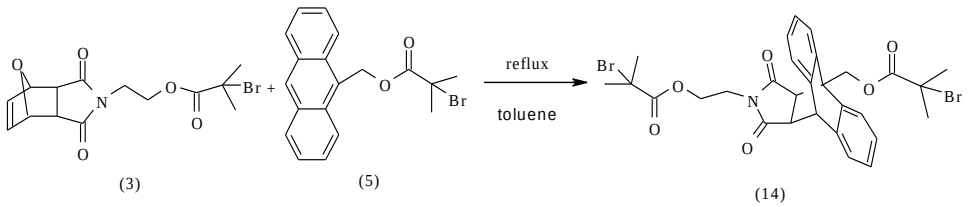


Figure 4.8. The ^{1}H NMR spectrum of PEG-anthracene in $CDCl_3$

4.5 Preperation of Block Copolymers by Diels-Alder Reaction:

The efficiency of model DA reaction was demonstrated between **3** and **5** in toluene at 110 ^{o}C.



4.14

First a retro-DA reaction of **3** occurred in order to give the deprotected maleimide functionality at reflux temperature of toluene. Then, DA reaction of this deprotected maleimide and **3** afforded the expected **5** in a quantitative yield (97%). ^{1} H NMR confirmed the structure of 5. From the spectrum, a complete disappearance of an aromatic proton of anthracene at 8.5 ppm and oxatricyclo vinyl signal at 6.5 ppm was observed. Moreover, new signals corresponding to CH_2 protons adjacent to anthracene ring at 5.6 ppm and a bridgehead proton of cyclo-adduct (CH) at 4.8 ppm were primarily detected. The ^{1}H NMR spectrum of model DA, **14,** is shown in Figure 4.9.

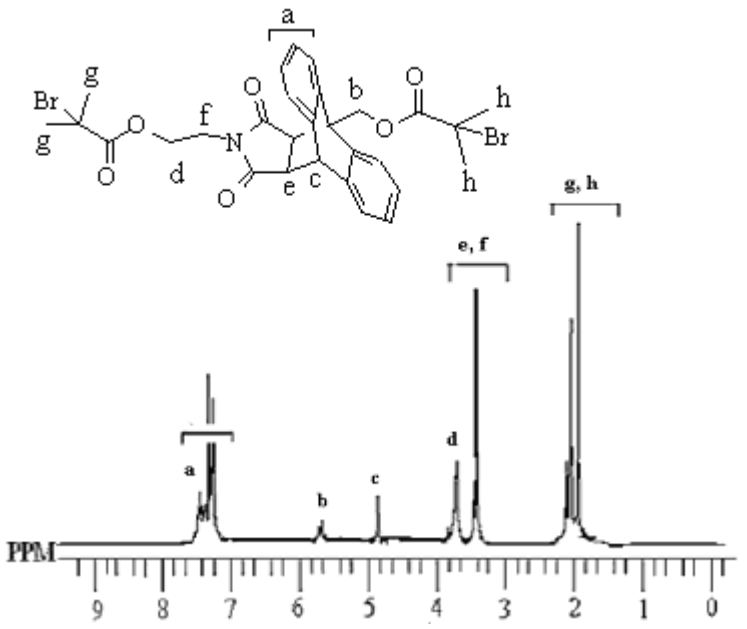


Figure 4.9. The ^{1}H NMR spectrum of Model DA in $CDCl_3$

Diels Alder adduct formation is also monitored by UV spectrophotometer. Because, compound 3, displays characteristic five-finger absorbance from 300 to 400 nm. However, 5 showed no absorbance in this region indicating that DA reaction occurred quantitatively. The UV spectrum of model DA, **14,** is shown in Figure 4.10.

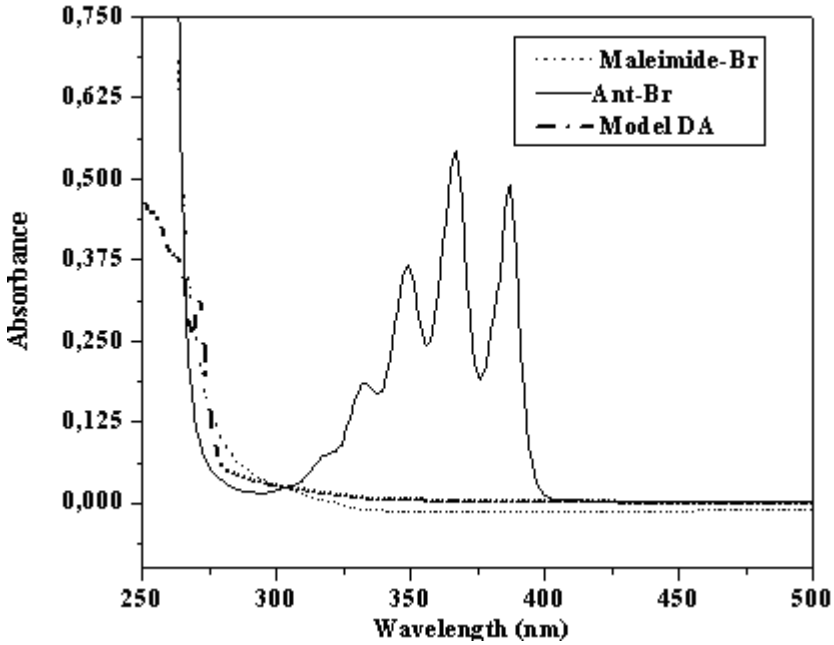


Figure 4.10. The UV spectrum of Model DA in CH_2Cl_2. Maleimide-Br ($4.9x10^{-5}$ M), Ant-Br ($5.4x10^{-5}$ M), Model DA ($6.97x10^{-5}$ M).

Using DA reaction strategy, a number of block copolymers were simply prepared by refluxing corresponding end functionalized polymers in toluene. Thus obtainedblock copolymers were purified by conventional methods described in experimental section prior to GPC and ^{1}H NMR measurements. The characteristics of anthracene- and maleimide-end functionalized polymers and their block copolymers were tabulated in Table 4.2.

Table 4.2. The characteristics of anthracene- and maleimide-end functionalized polymers and their block copolymers by DA reaction.

Polymer	$M_{n,theo}$	$M_{n,NMR}$	$M_{n,UV}$	$M_{n,GPC}$[e]	M_w/M_n[e]
PS-anthracene	3240	3240	3430	3400	1.13
PEG-maleimide	750	*720*	-	740	1.07
P*t*BA-maleimide	2560	2600	-	3500	1.16
PEG-anthracene	5300	5360 4100	4800	5300	1.13
PEG-*b*-PS	3990[c]	(3690)[d] 8850	-	4700	1.07
PMMA-*b*-PS[a]	6040[c]	(9450)[d] 5350	-	9500	1.13
P*t*BA-b-PS	5800[c]	(5840)[d] 11150	-	4400	1.30
PMMA-b-PEG[b]	7600[c]	(10860)[d]	-	8500	1.11

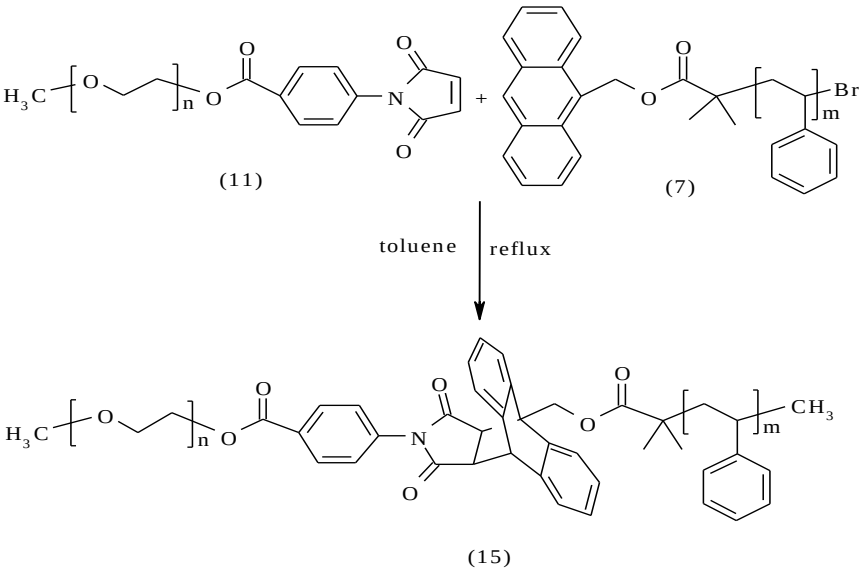
[a] PMMA-maleimide was obtained from run no 2 in Table 1. [b] PMMA-maleimide was obtained from run no 1 in Table 1.

[c] Calculated from a sum of Mn,theo values of corresponding homopolymers.

[d] Calculated from a sum of Mn,NMR values of corresponding homopolymers.

[e] Calculated from GPC calibrated with linear polystyrene standarts.

Thus, PEG-maleimide and PS-anthracene were allowed to react at 110 ^{o} C in order to give PEG-PS block copolymer.



4.15

The efficiency of DA reaction was monitored by UV spectroscopy following the disappearance of anthracene moiety. A calculation for DA efficiency was based on molar absorptivity coefficient of **5**(ε = 9451 at 366 nm in CH_2Cl_2). The efficiency was found to be 97.5%. The UV spectrum of PS-*b*-PEG, **15,** is shown in Figure 4.11.

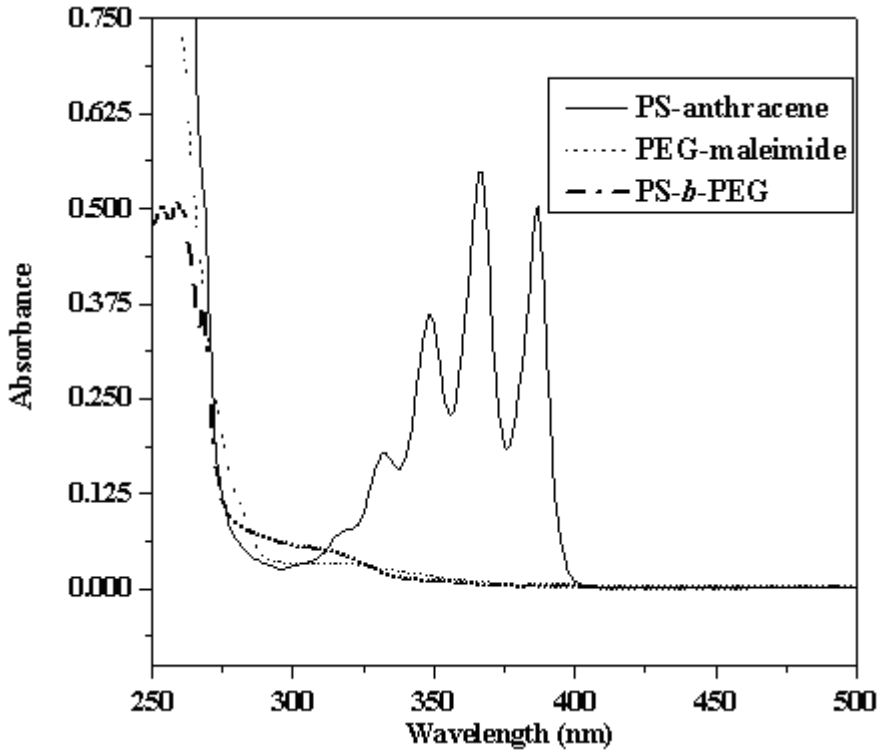


Figure 4.11. The Uv spectrum of PS-*b*-PEG in CH_2Cl_2. PS-anthracene (4.7×10^{-5} M), PEG-MI (6.2×10^{-5} M), PS-*b*-PEG (5.71×10^{-4} M).

Moreover, $M_{n,NMR}$ of PEG-PS block copolymer was determined by comparing of the integrals of the -OCH_2CH_2 protons of PEG at 4.4-3.3 ppm and that of the aromatic protons of PS at 6.5-7.5 ppm. The ^{1}H NMR spectrum of PS-*b*-PEG , **15,** is shown in Figure 4.12.

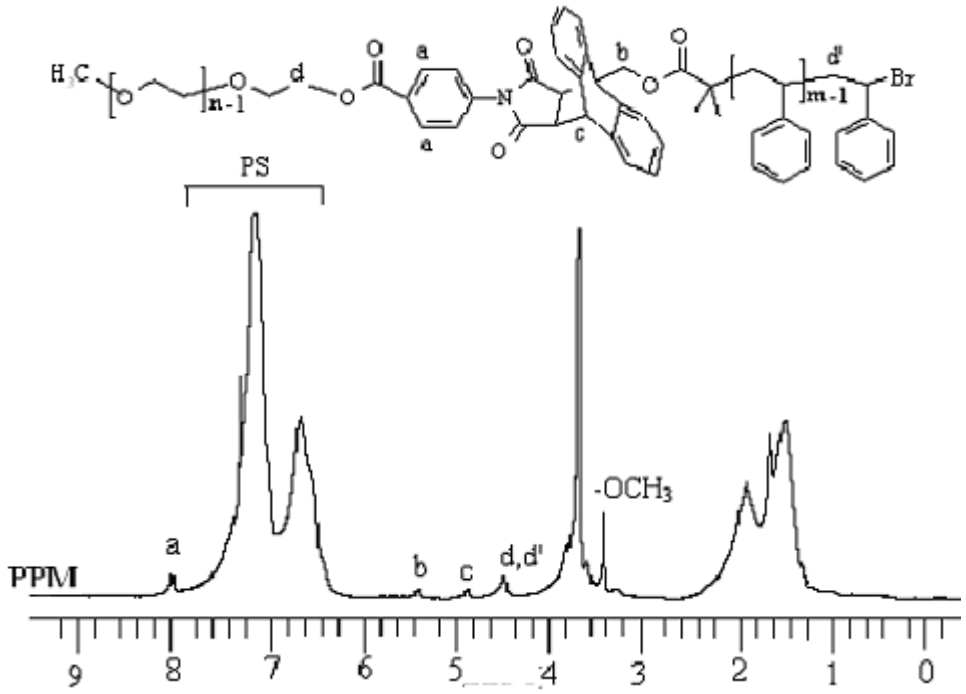


Figure 4.12. The ^{1}H NMR spectrum of PS-*b*-PEG in $CDCl_3$

GPC traces of block copolymer were unimodal and no tailing was observed in the molecular weight of precursors. GPC traces of PS-anthracene, PEG-maleimide and PS-*b*-PEG were shown in Figure 4.13.

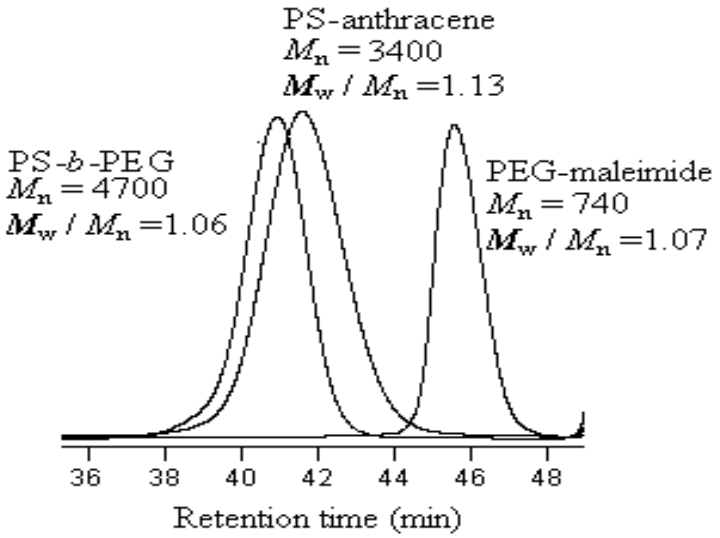
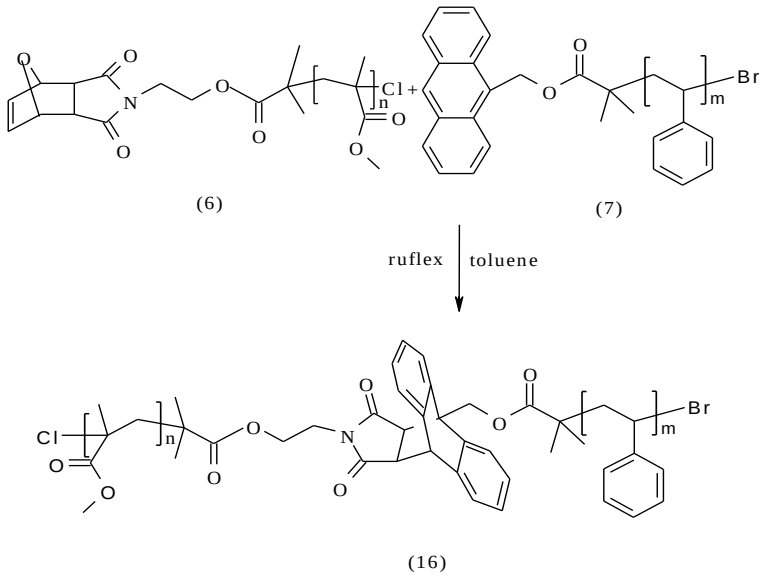


Figure 4.13. GPC of PS-anthracene, PEG-maleimide and PS-*b*-PEG in THF

Next, PMMA-PS block copolymer was simply obtained by toluene refluxing of PMMA-maleimide and PS-anthracene. Here, furan protected maleimide-end functionality was deprotected (retro-DA) at toluene reflux temperature and subsequently block copolymerization (DA reaction) occurred.



4.16

The efficiency of Diels-Alder reaction based on UV measurement was determined 98.5 % according to a procedure described previously. The UV spectrum of PMMA-*b*-PS, **16,** is shown in Figure 4.14.

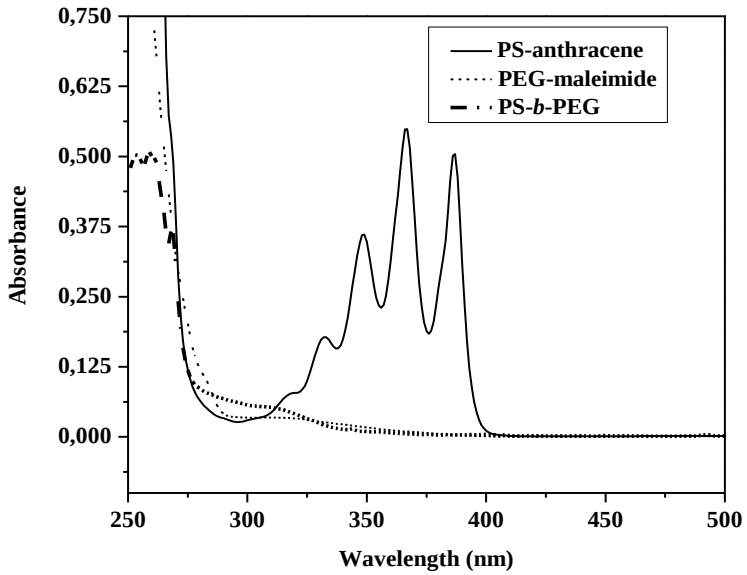


Figure 14. The UV spectrum of PMMA-*b*-PS in CH_2Cl_2. PMMA-maleimide (5.2 $x10^{-5}$ M), PS-anthracene (4.7 $x10^{-5}$ M), PMMA-*b*-PS (5.8 $x10^{-5}$ M).

$M_{n,NMR}$ of PMMA-PS block copolymer was also determined by comparing of the integrals of the –OCH3 protons of PMMA at 3.6 ppm and that of the aromatic protons of PS at 6.5-7.5 ppm. The ^{1}H NMR spectrum of PMMA-*b*-PS , **16,** is shown in Figure 4.15.

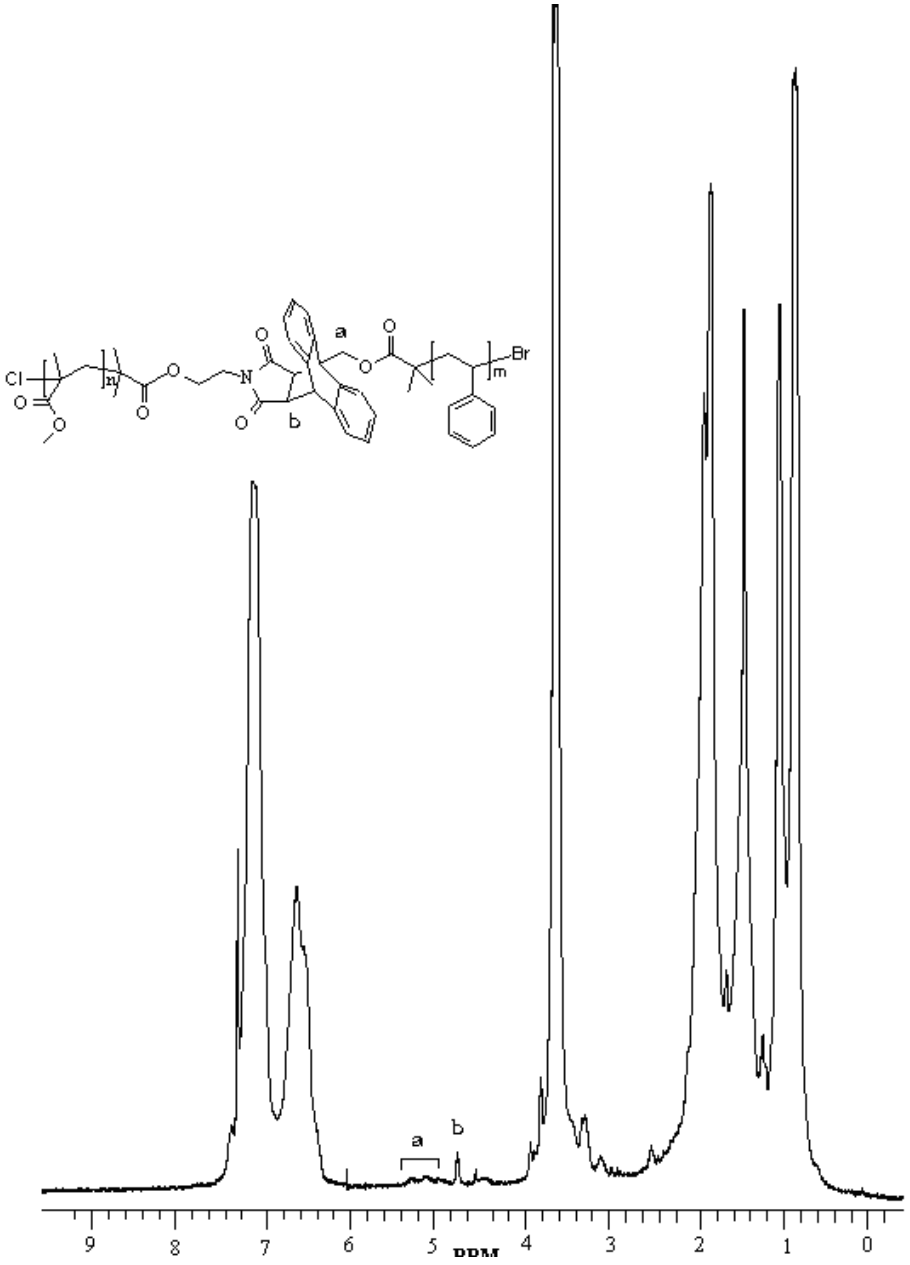


Figure 4.15. The ^{1}H NMR spectrum of PMMA-*b*-PS in $CDCl_3$

A shift of PS-anthracene and PMMA-maleimide precursors to higher molecular weight region revealed that the formation of PS-b-PMMA by Diels-Alder reaction was achieved successfully. GPC traces of PMMA-maleimide, PS-anthracene and PMMA-b-PS were shown in Figure 4.16.

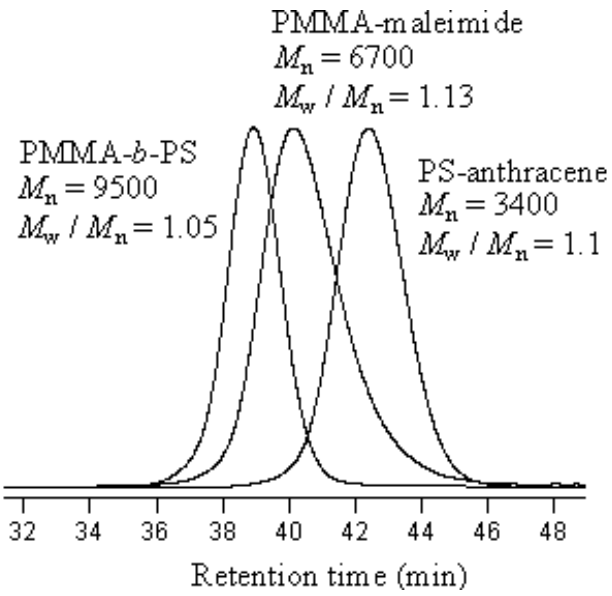
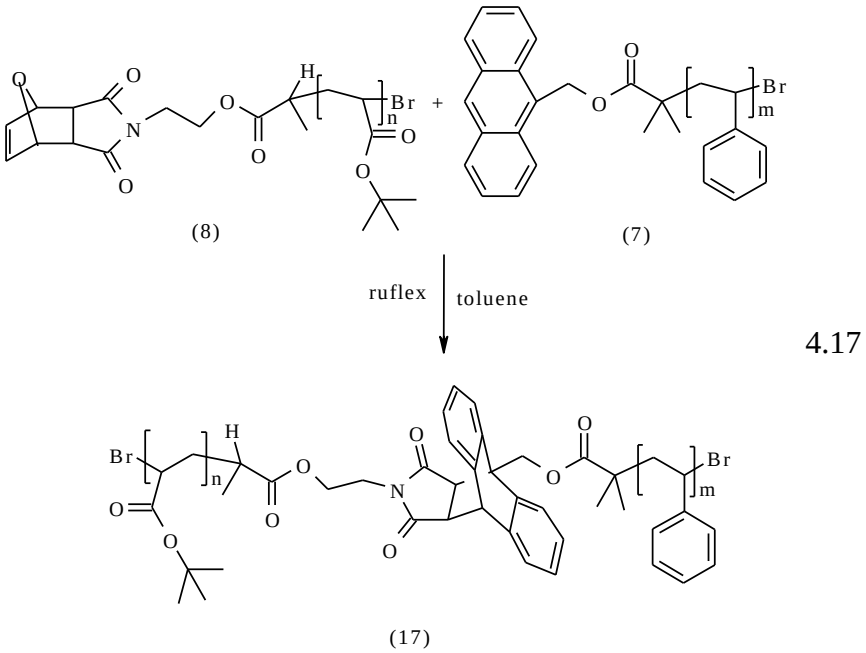


Figure 4.16. GPC of PMMA-maleimide, PS-anthracene and PMMA-*b*-PS in THF

P*t*BA-PS block copolymer was prepared by using a similar procedure.



4.17

In this reaction, P*t*BA-maleimide, PS-anthracene and PtBA-*b*-PS were measured by UV spectrometer and compound **7**, displays characteristic five-finger absorbance from 300 to 400 nm. However, **17** showed no absorbance in this region indicating that Diels-Alder reaction occurred quantitatively. Diels-Alder block copolymerization efficiency was also determined by UV measurement and found as 92 %. The UV spectrum of P*t*BA-maleimide, PS-anthracene and P*t*BA-*b*-PS are shown in Figure 4.17.

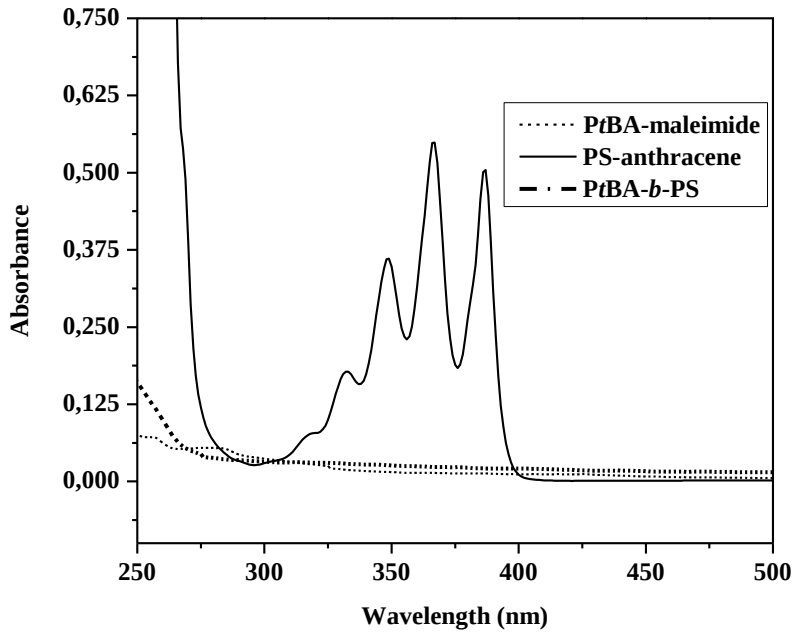


Figure 4.17. The UV spectrum of P*t*BA-*b*-PS in CH_2Cl_2. P*t*BA-maleimide (4.5 x10^{-5} M), PS-anthracene (4.7 x10^{-5} M), P*t*BA-*b*-PS (5.5 x10^{-5} M).

$M_{n,NMR}$ value of P*t*BA-*b*-PS block copolymer was calculated by comparing the integrals of aromatic group signals of PS (6.5-7.5 ppm) nad that of the *tert-butyl* signal of P*t*BA (1.4 ppm). The ^{1}H NMR spectrum of P*t*BA-*b*-PS , **17,** is shown in Figure 4.18.

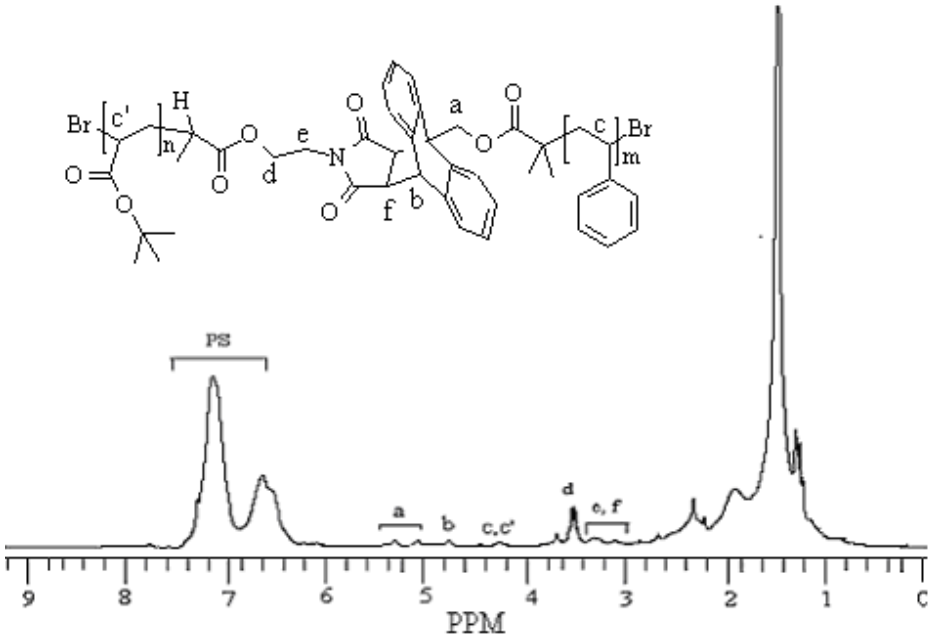


Figure 4.18. The ^{1}H NMR spectrum of P*t*BA-*b*-PS in $CDCl_3$

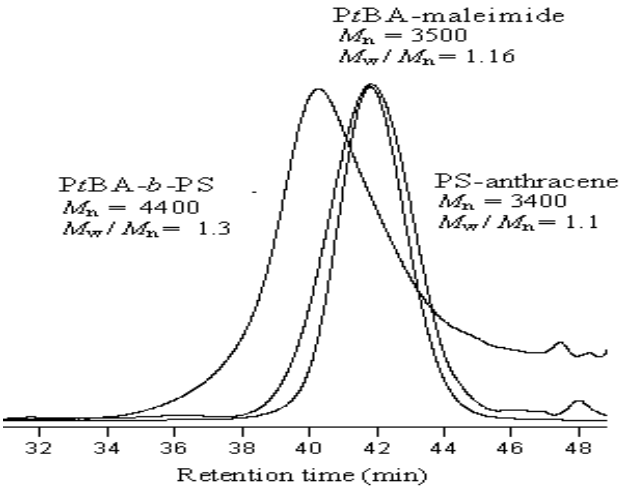
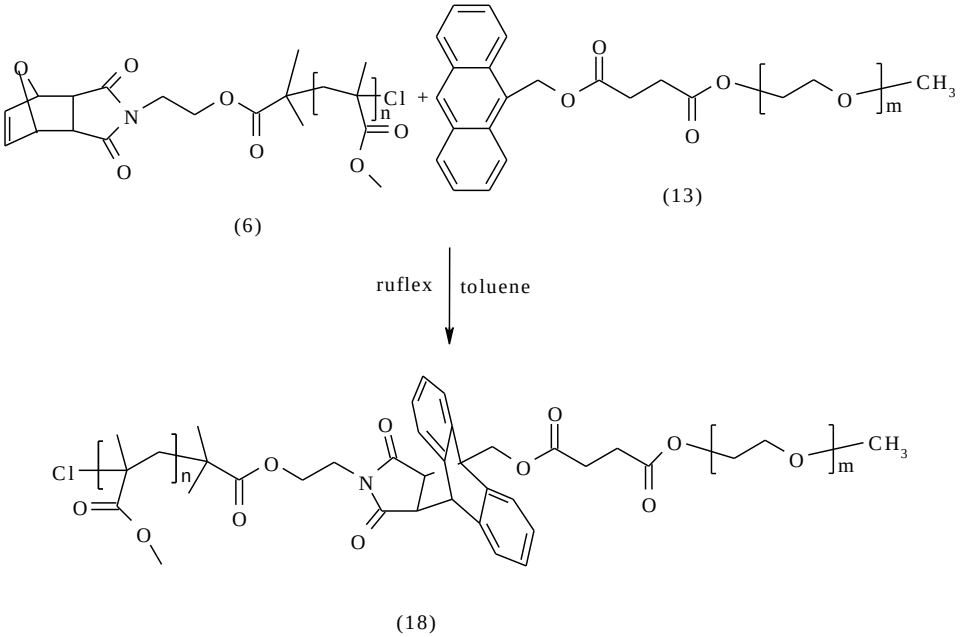


Figure 4.19. GPC of P*t*BA-maleimide, PS-anthracene and P*t*BA-*b*-PS in THF

In the final Diels-Alder block copolymerization, PMMA- PEG block copolymers was synthesized as a similar procedure. Diels-Alder block copolymerization efficiency was determined by UV measurement and found as 93 %. IN the case of PMMA-*b*-PEG, molar absorptivity coefficient of **13** (ε = 11524 at 366 nm in CH_2Cl_2) was used for calculation of Diels-Alder efficiency. In this reaction, PMMA-maleimide, PEG-anthracene and PMMA-*b*-PEG were measured by UV spectrometer and compound **13**, displays characteristic five-finger absorbance from 300 to 400 nm. However, **18** showed no absorbance in this region indicating that Diels-Alder reaction occurred quantitatively. The UV spectrum of PMMA-maleimide, PEG-anthracene and PMMA-*b*-PEG are shown in Figure 4.20.



4.18

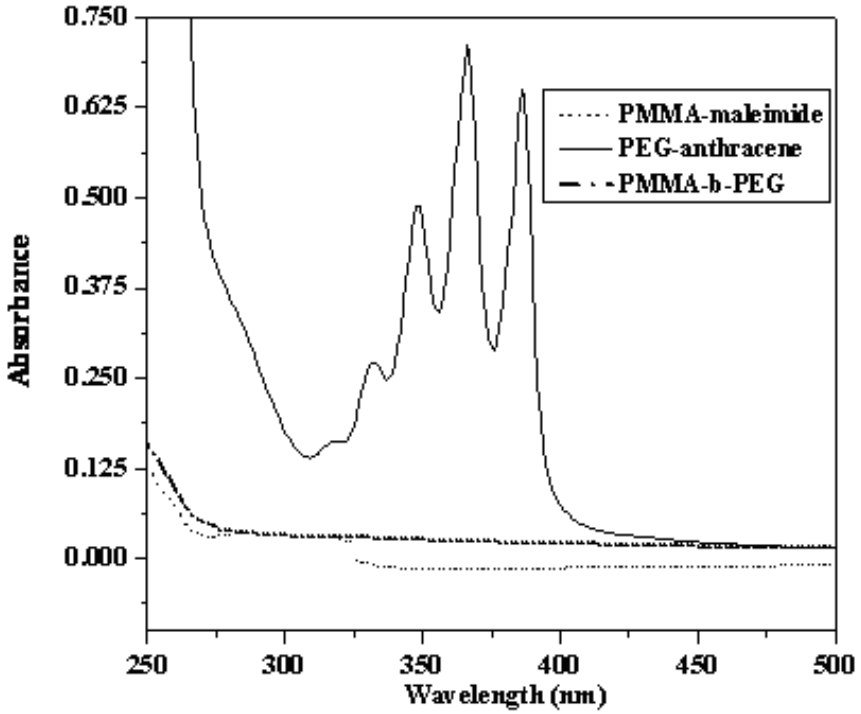


Figure 4.20. The UV spectrum of PMMA-*b*-PEG in CH_2Cl_2. PMMA-maleimide (5.2 x10^{-5} M), PEG-anthracene (7.5 x10^{-5} M), PMMA-*b*-PEG (4.9 x10^{-5} M).

$M_{n,NMR}$ values of PMMA-PEG block copolymer was determined by comparing of integrals of $-OCH_3$ signal of PMMA (3.57 ppm) and that of the $-CH_2CH_2O$ signal of PEG (3.62 ppm), respectively. The ^{1}H NMR spectrum of PMMA-*b*-PEG , **18,** is shown in Figure 4.21.

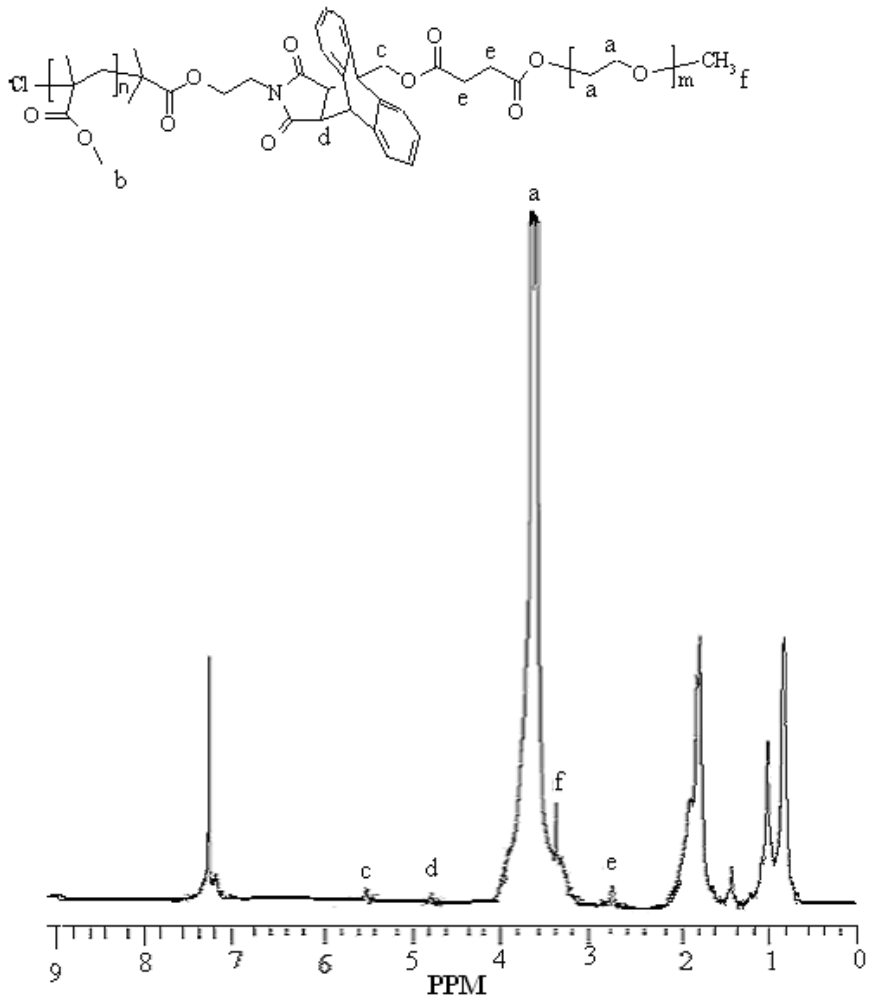


Figure 4.21. The ^{1}H NMR spectrum of PMMA-*b*-PEG in $CDCl_3$

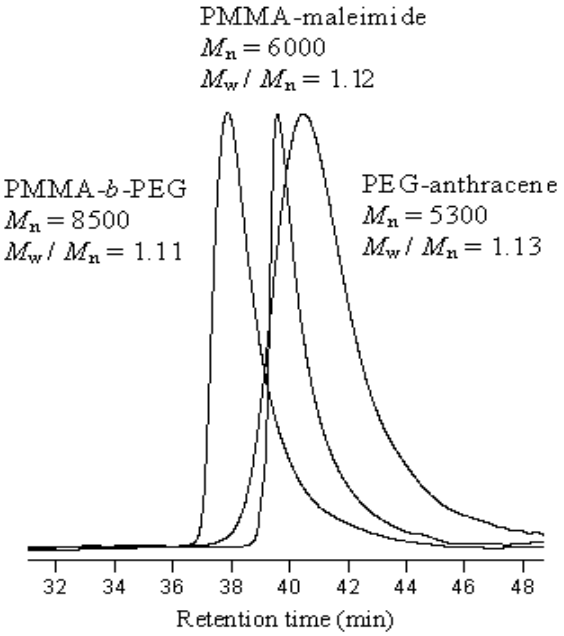


Figure 4.22. GPC trace of PMMA-*b*-PEG in THF

4.6 Differantial Scanning Calorimetry:

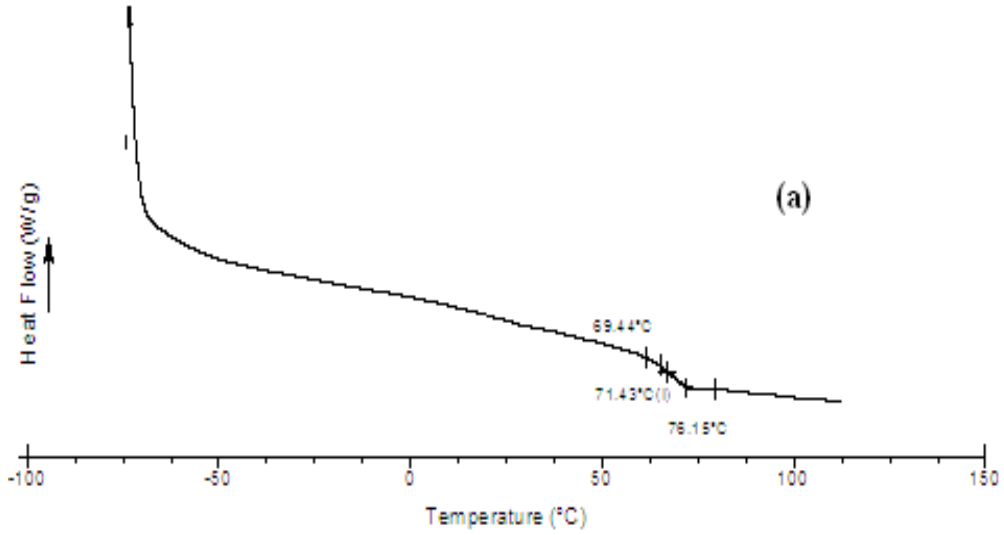


Figure 4.23. DSC termogram of (a) PS-*b*-PEG

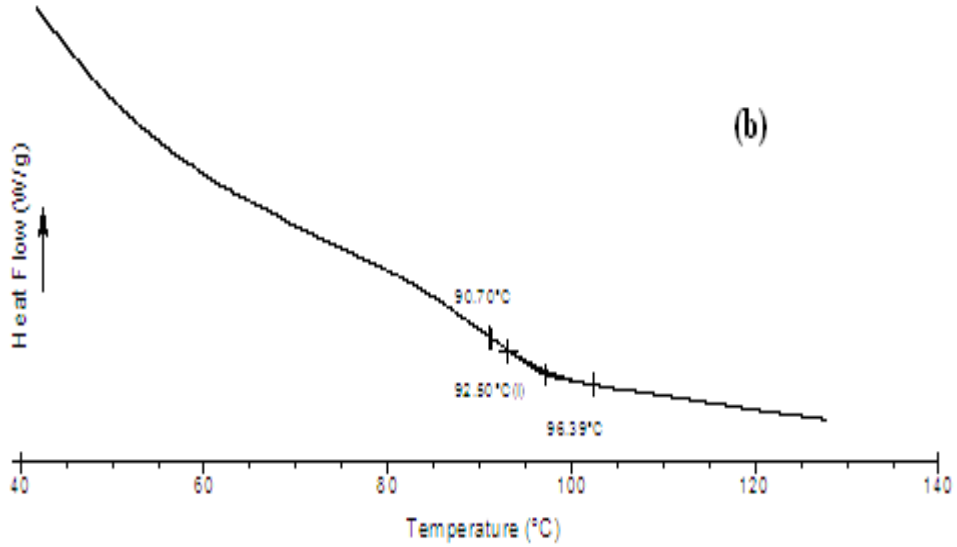


Figure 4.24. DSC termogram of (b) PMMA-*b*-PS

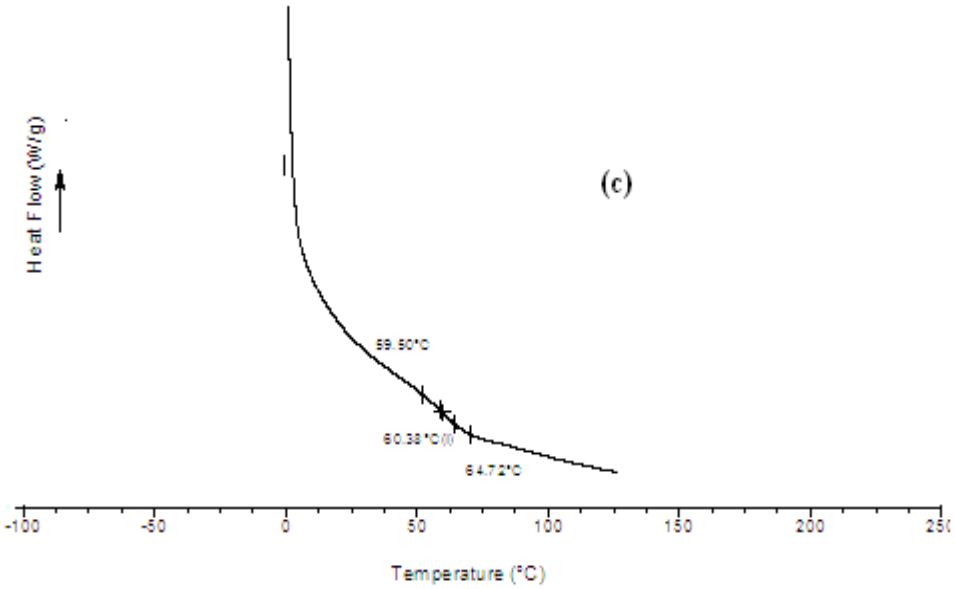


Figure 4.25. DSC termogram of (c) P*t*BA-*b*-PS

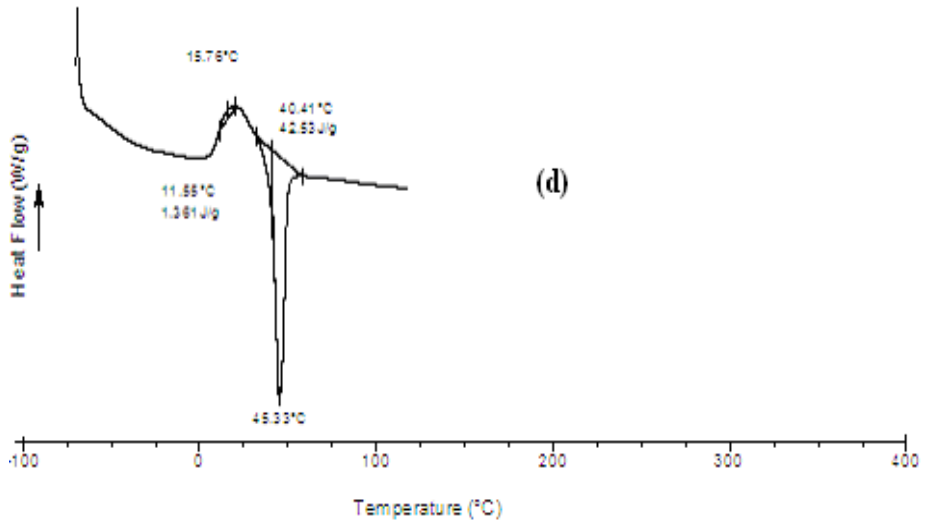


Figure 4.26. DSC termogram of (d) PMMA-*b*-PEG

The thermal behavior of the polymers was investigated by Differantial scanning calorimetry (DSC) measurements. DSC was used to observe the endothermic and exothermic transitions during the polymerization reaction. **(**Figure 23). The PS-*b*-PEG copolymer **(a)** displayed a glass-transition at 71.43 ^{o} C, which was consistent with that of PSt homopolymer. Any Tg regarding with PEG segment was not observed, due to the relatively shorter PEG compared with PSt segment. The PMMA-*b*-PS copolymer **(b)** displayed one transition at 92.50 ° C, that is the glass-

transition temperature (T_g). The P*t*BA-*b*-PS copolymer **(c)** displayed only one transition at 60.38° C, that is the glass-transition temperature (T_g). In this thermograms of block copolymers **(a), (b)**, and **(c),** there was no sign of melting transitions. The PMMA-*b*-PEG **(d)** copolymer displayed a glass- transition (T_g) at 45.33 ^{o} C and melting transition (T_m) at 15.76 ^{o} C. All DSC scanning was repeated two times to confirm the obtained data. For the study of the thermal behavior of PS-*b*-PEG **(a)**, PMMA-*b*-PEG copolymers **(d)** themselves, samples were equilibrated at -70 ° C and were heated to 140°C at a heating rate of 10 ° C/min in a closed cell. However, PMMA-*b*-PS copolymer **(b)** was equilibrated at 25 ° C and was heated to 140 ° C at a heating rate of 10°C/min in a closed cell. P*t*BA-*b*-PS copolymer **(c)** was equilibrated at 0 ° C and were heated to 140 ° C at a heating rate of 10°C/min in a closed cell.

11. CONCLUSION

In this work, we showed a simple and an effective method fort he preparation of block copolymers by DA reaction between maleimide- and anthracene-end functionalized polymers. The block copolymerization was carried out at reflux temperature of toluene. In some cases, nly by-product is an easily removable furan. It was found that the efficiencies of DA reaction were higher than 92 % for all cases. All homopolymers have the controlled molecular weight, well-defined chain ends and low polydispersity. Therefore, the block copolymers PMMA-*b*-PS, PEG-*b*-PS, P*t*BA-*b*-PS, and PMMA-*b*-PEG displayed similar characterisrics.

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